INSTITUTO POLITÉCNICO DE BRAGANÇA
Escola Superior de Tecnologia e Gestão

# Development of Water-Borne Adhesives using Monomers from Renewable Sources

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"*Escola Superior de Tecnologia e Gestão de Bragança"* for obtain the master's degree in Chemical Engineering

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***Dedicated to my parents (Manuel António Pimenta and Maria Rosa Gonçalves), because without their support I would never have achieved this goal in my life.***

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## Abstract:

Within this master thesis, I carried out an experimental investigation of new synthetic routes to acrylic aqueous adhesives using components obtained from renewable raw materials. The experimental program has included two different strategies. In the first strategy we investigated the covalent incorporation of carboxylic acids coming from vegetable oils into methacrylic monomer and their subsequent miniemulsion polymerization. Our second strategy consisted in the incorporation of similar carboxylic acids into methacrylic monomers via ionic complexation. Then, we investigated a serie of polymer latexes synthesized via free radical emulsion polymerization of these ionic monomers.

In the case of our covalently attached monomer, it was possible to obtain high efficiency of the miniemulsion polymerization reaction. However, we observed some coagulation problems of the latexes and the obtained film were brittle and did not show adhesive properties.

In the second case, we investigated the polymerization of the ionic methacrylic-carboxylate monomers in water by free radical polymerization. For this system it was observed that an exact range exists between the monomer solids content of the reaction and the ratio between the monomer components, in order to obtain stable emulsions. Interestingly, after drying, the obtained films showed good adhesive properties demonstrating a remarkable ability of these to adhere in rigid surfaces.

**Keywords:** Adhesives, ionic liquids, carboxylic acids, free radical polymerization, emulsion, miniemulsion.

## Sumário:

Nesta tese de mestrado, realizei uma investigação experimental de novas rotas de síntese para formular adesivos acrílicos em fase aquosa usando componentes obtidos a partir de matérias-primas renováveis. O programa experimental incluiu duas estratégias distintas. Numa primeira estratégia foi investigada a incorporação covalente de ácidos carboxílicos provenientes de óleos vegetais em monómeros metacrílicos e sua subsequente polimerização por miniemulsão. A segunda estratégia consistiu na incorporação de ácidos carboxílicos similares, em monómeros metacrílicos, via complexação iónica. Em seguida realizou-se uma investigação de uma serie de "*latexes*" de polímeros, obtidos por polimerização em emulsão de radicais livres provenientes destes monómeros iónicos.

No caso do monómero ligado covalentemente, foi possível obter uma elevada eficiência da reacção de polimerização por miniemulsão. No entanto, observaram-se alguns problemas de coagulação dos "*latexes*" e os filmes obtidos eram quebradiços não apresentando quaisquer propriedades adesivas.

No segundo caso estudado, foi investigada a polimerização dos monómeros iónicos metacrílicos-carboxilatos em água por polimerização via radical livre. Para este sistema verificou-se que existe uma faixa exacta entre o teor de sólidos contidos do em reacção e a razão mássica entre os componentes monoméricos, a fim de se obterem emulsões estáveis. Curiosamente, após a secagem dos filmes obtidos, estes apresentaram boas propriedades adesivas que demonstram uma notável capacidade destes compostos para aderir a superfícies rígidas.

**Palavras-chave:** Adesivos, líquidos iónicos, ácidos carboxílicos, polimerização via radical livre, emulsão, miniemulsão.

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## Nomenclature

[A] – Concentration of specie A (mol/L), A = I, M.

AIBA – 2,2'- Azobis (2- methylpropionamide) dihydrochloride.

AN – Acid Number.

ASA – Ascorbic acid.

BTC – 1,3,5-Bencenetricarboxilic acid.

$CDCl_3$ – Deuterated chloroform.

$d_d$ – Droplet size.

DMAEA – 2-(dimethylamino)ethyl acrylate.

DMAEMA – 2-(dimethylamino)ethyl methacrylate.

dp – Particule size.

$D_2O$ – Deuterated oxide.

Dowfax 2A1 – Alkyldiphenil oxide disulfonate.

*f* – Efficiency of the initiator.

FRP – Free Radical Polymerization.

FTIR – Fourier Transform Infra-Red Spectroscopy.

I – Initiator.

ILs – Ionic Liquids.

$K_i$ – Constants for initiator decomposition, *i = d, p, t.*

KOH – Potassium hydroxide.

KPS – Potassium persulfate.

M – Monomer.

$M_w$ – Weight-average molecular weight.

$N_2$ – Nitrogen.

NMR – Nuclear Magnetic Resonance;

PILs – Poly (Ionic Liquids).

PP – Polypropylene.

R· – Free Radical;

$RM_n$· – Growing polymer chain, n=number of repeating units.

rpm – Rotations per minute.

SAFT – Shear adhesion failure temperature.

SC – Solid contents.

TBHP – Tert-butyl hydroperoxide.

Tg – Glass transition temperature.

Wt% – Total weight percentage.

# Chapter 1

## 1.1 Introduction:

In general, adhesive is defined like “a substance capable of holding materials together by surface attachment”. This is a simple definition for a material that is the basis of a multi-million dollar industry with more than 750 companies competing for a share in the market.[1]

Prior to the twentieth century, practically all adhesives were derived from plant or animal sources, such us animal glues, fish glue, casein glue, starch, cellulose adhesives, rubber-based solvent cements, epoxies adhesives and hot melt adhesives. In our days the progress in organic chemistry and an increase in demand for adhesives led to the development of synthetic compounds, characterized for high technology and/or complicated chemical processes.[1, 2]

However, today the world is faced with major environmental challenges such as global warming, the increasing emissions of green house gases, and the recognized depletion of the earth limited petroleum reserves. The growing awareness of society toward environmental issues combined with the recent government’s regulations and incentives toward the reduction of carbon dioxide emission is pushing the chemical industry to develop greener products and find alternatives growth strategies based on sustainable economic models.[3]

Several arguments point the great potential of renewables sources used like raw materials as an alternative for the production of polymeric materials. Carboxylic acids are widespread in nature and are important raw materials for the synthesis of polymers. In case of the synthesis of adhesives, carboxylic acid groups can improve the wetting onto the adherent surface and accelerate the rate of bond establishment (tack) via the formation of hydrogen bonding, non-covalent interactions, or both. Intra- and intermolecular hydrogen bonding interactions between carboxylic acid-functional polymer chains also induce remarkable modifications to the bulk properties of the adhesive (cohesion, viscoelasticity, etc.) and therefore influence its adhesive properties.[3, 4]

The aim of this project was to report the development and characterization of adhesives using renewable sources. The synthesis was realized by two different routes from covalent incorporation of carboxylic acids, derived from vegetable oils, and ionic incorporation of them. The polymerizations were performed by different carboxylic acids. The final product obtained was characterized by different methods and the adhesive properties of them were investigated. The synthesis was carried out by emulsion and miniemulsion polymerization by transfer of free radicals.

## 1.2 Organization of the Dissertation:

Chapter 1 intends to introduce the topic of this thesis in the current framework and present the primary aim of the project. In Chapter 2 some general concepts about the theme, and the different methods for the synthesis used in experimental part of this project are described.

Chapter 3 is intended for the exposure of the main equipment and reagents to be used in the course of scientific research.

Chapter 4 presents the results obtained in some experiments, using different analyses.

Chapter 5 contains a brief conclusion about all work and Chapter 6 presents the bibliographic references.

# Chapter 2

## 2.1 General concepts about Poly Ionic Liquids (PILs):

ILs generally are defined as organic/inorganic salts with low melting point, good chemical and electrochemical stability, low flammability, negligible vapor pressure and high ionic conductivity. ILs are chemically composed of an organic asymmetric cation (e.g. imidazolium, pyridinium, or tetraalkylammonium) and an inorganic anion such as halide, tetrafluoroborate, hexafluorophophate, etc. By polymerization of ILs we have a new class of polymers called poly (ionic liquids) (PILs), which have the unique properties of ILs together with the intrinsic polymer properties. Typically PILs can be classified as polycations bearing a cation in the backbone's part of monomer unit, polyanions bearing an anion or polyzwitterions having both anion and cation (Figure 1). Actually, PILs can be used in different areas such as biosensors, supports of catalysts, polymeric surfactants, polymer electrolytes and among other's.[6, 7]

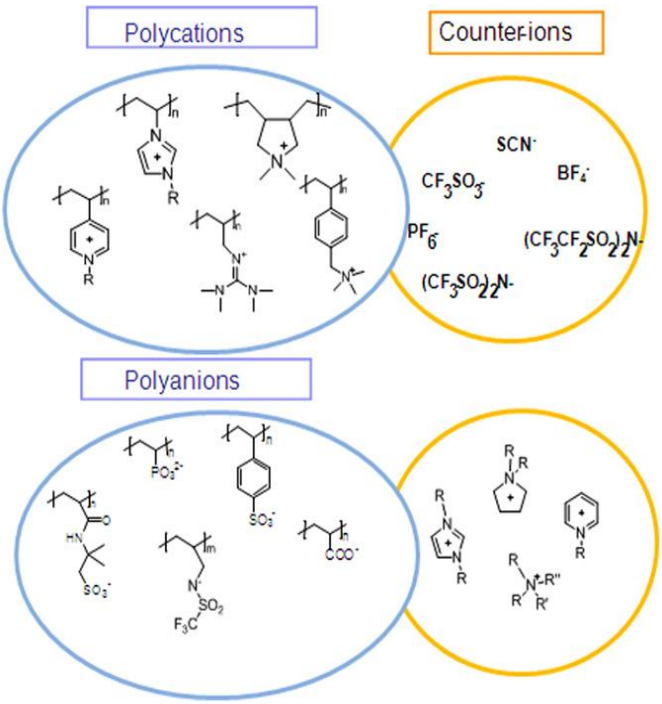



**Figure 1:** Representative chemical structures of PILs.[6]

The synthesis of polymers materials from carboxylic acid can be mediated for the introduction of new ionic moieties, cations and anions, coming from ionic liquids (ILs) chemistry. [4]

Actually, the investigation of this kind of synthesis, to develop new materials obtained from the incorporation of renewable products, is thus of a growing interest because of the high price of the ionic liquids in the market.

During this experimental work was investigated the development of an adhesive based on this type of synthesis.

## 2.2 Methods of the Synthesis:

### 2.2.1 Free Radical Polymerization:

In the experimental part of this work polymers were synthetized by Free Radical Polymerization (FRP). This method is widely used in industrial practice in both homogeneous (bulk and solutions) and heterogeneous (solution and emulsion) processes, largely due to its mild reaction conditions. FRP can be in fact easily operated in the presence of impurities, such as residuals of inhibitor and oxygen traces, and in a large range of temperature. However, this kind of polymerization has some limitations such as the lack of control of the polymer molecular weight and the inability to produce block copolymers.[8]

#### 2.2.1.1 Mechanism of FRP:

Free Radical polymerization is a method of polymerization by the successive addition of free radical building blocks. Free radicals can be formed via a number of different mechanisms usually involving separate initiator molecules. Following its generation, the initiating free radical adds monomers units, thereby growing the polymer chain. FRP can be described in different steps:

- **Initiation:** Is the first step of the polymerization process. During the initiation, an active center is created from which a polymer chain is generated. Initiation has two steps. In the first step one or two radicals are created from the initiating molecules. In the second step, radicals are transferred from initiator molecules to the monomer units present.[9]

During this project, experiments with different initiators were performed: a thermal initiators such as, AIBA (2,2'- Azobis (2- methylpropionamide) dihydrochloride, purity 97%, was purchased by Sigma-Aldrich) this one is an azo difunctional compound, and KPS (Potassium persulfate, purity 99%, was purchased by Sigma-Aldrich). The other type of initiator used in this project was a redox initiator TBHP-ASA (tert-butyl hydroperoxide, 70 wt% in $H_2O$, was purchased by Sigma-Aldrich; and Ascorbic acid, purity 99%, was purchased by Panreac). Figure 2 illustrates the molecular and

structural formula of the compounds mentioned before and in Table 1 is presented a compilation about their properties.

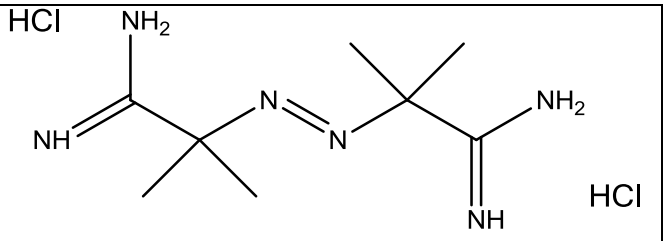
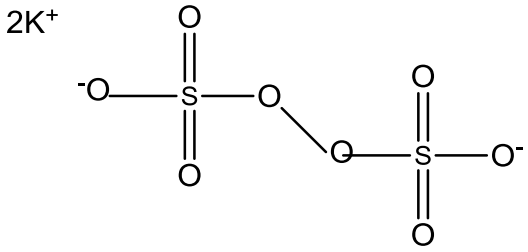
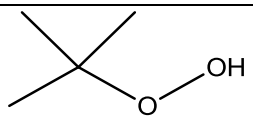
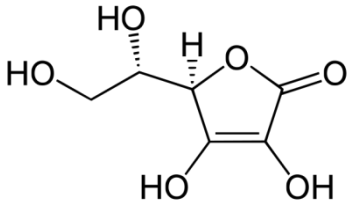
| | | |
|---|---|---|
| **AIBA** | **Molecular Structure** |  |
| | **Molecular Formula** | $C_8H_{20}N_6Cl_2$ |
| **KPS** | **Molecular Structure** |  |
| | **Molecular Formula** | $K_2S_2O_8$ |
| **TBHP** | **Molecular Structure** |  |
| | **Molecular Formula** | $C_4H_{10}O_2$ |
| **ASA** | **Molecular Structure** |  |
| | **Molecular Formula** | $C_6H_8O_6$ |

**Figure 2:** Illustration of molecular and structural formula of the different initiators used in experimental part of this project.

**Table 1:** Properties of the different initiators used in the experimental part of this project.

| Compound | Properties | Units | Conditions | Valor |
|---|---|---|---|---|
| **AIBA** | Molecular Weigh | $gmol^{-1}$ | - | 271.19 |
| | Solubility | Water, methanol, acid solutions | | |
| | Insolubility | Toluene | | |
| | Activity Energy | $KJmol^{-1}$ | - | 124 |
| | Melting Point | ˚C | - | 170-175 |
| | Decomposition Temperature | ˚C | - | 56 |
| | Boiling Point | ˚C | 760 mmHg | 267 |
| | Half-Life | Hours | - | 10 |
| **KPS** | Molar Mass | $gmol^{-1}$ | - | 270.322 |
| | Density | $gcm^{-3}$ | - | 2.477 |
| | Solubility | Water | | |
| | Insolubility | Alcohol | | |
| | Melting Point | ˚C | - | < 100 |
| | Refractive Index | - | - | 1.467 |
| **TBHP** | Molar Mass | $gmol^{-1}$ | - | 90.12 |
| | Density | $mgcm^{-3}$ | - | 935 |
| | Melting Point | ˚C | - | -3 |
| | Boiling Point | ˚C | - | 37 |
| | Solubility | Water | | |
| | Refractive Index | - | - | 1.387 |
| **ASA** | Molar Mass | $gmol^{-1}$ | - | 176.12 |
| | Density | $gcm^{-3}$ | - | 1.65 |
| | Melting Point | ˚C | - | 190-192 |
| | Solubility | Water, ethanol, glycerol, propylene glycol | | |
| | Insolubility | Diethyl ether, chloroform, benzene, petroleum ether, oils, fats | | |

In the case of thermal decomposition, the initiator is heated until a bond is homolytically cleaved, producing two radicals, this kind of initiators should be used within appropriate temperature range (common temperature range is between 50 and

70 ˚C), and the most common choice in this type of the system is an initiator soluble in water. Figure 3 represents the formation of radicals in the case of initiator KPS for thermal degradation.

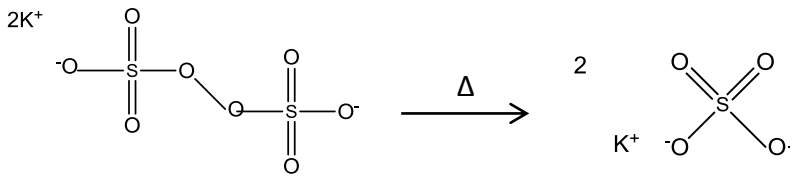



**Figure 3:** Thermal degradation of initiator KPS.

In redox reactions occurs the reduction of hydrogen peroxide or an alkyl hydrogen peroxide by iron. In this kind of systems occurs a high radical generation rates even at low temperatures (20-30˚C), the concentration of the initiator in the reactor decreases rapidly and, because of this, at least one (or both) of the redox components should be continuously added into the reactor. Figure 4 represents the formation of radical initiators of TBHP-ASA by a redox reaction.

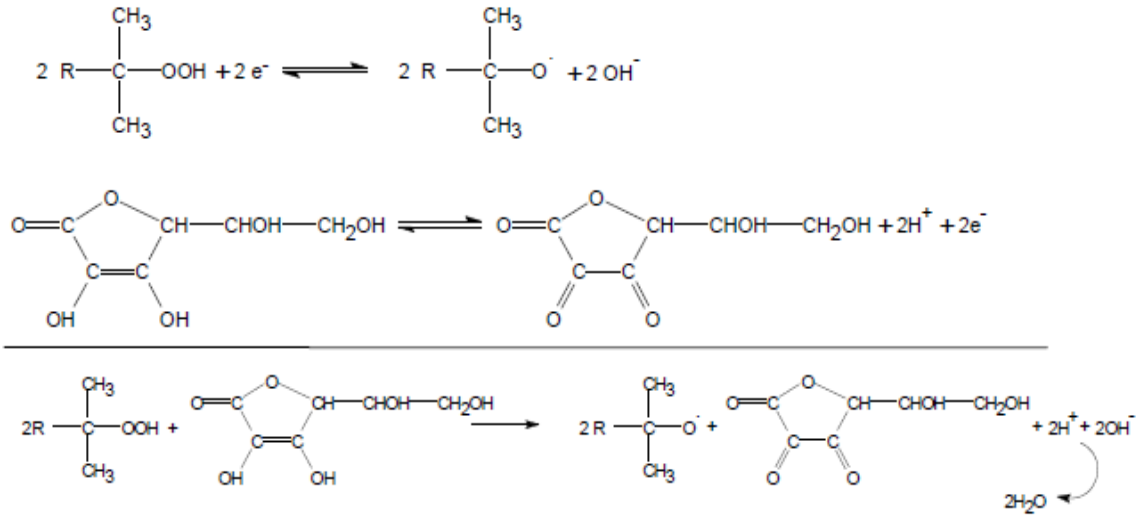


**Figure 4:** Redox reaction of initiator TBHP-ASA.

- **Propagation:** This step occurs during the polymerization. After the radical initiator is formed, it attacks a monomer.[10] Free radical uses one electron from the pi bond to form a more stable bond with a carbon atom. The other electron returns to the second carbon atom, turning the whole molecule into another radical. This begins the polymer chain. Once a chain has been

initiated, the chain propagates until there is no more monomer (living polymerization) or until termination occurs. There may be anywhere from a few to thousands of propagation steps depending on several factors such as radical and chain reactivity, the solvent, and temperature.[11,12]

- **Termination:** The chain termination will occur unless the reaction is completely free of contaminants. In this case, the polymerization is considered to be a living polymerization because propagation can continue if more monomer is added to the reaction. Living polymerization is most common in ionic polymerization, due the high reactivity of radicals. The termination can occur by several different mechanisms.[13]

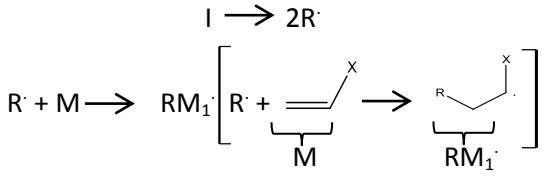
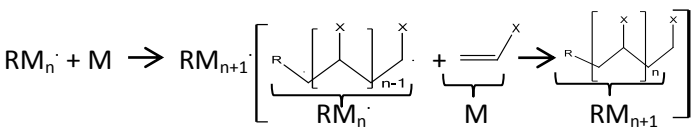
    1. Combination of two active chain ends, by combination or radical disproportionation.
    2. Combination of an active chain end with an initiator radical.
    3. Interactions with impurities or inhibitors; a common inhibitor is for example the presence of oxygen inside the reaction because if the growing chain will react with molecular oxygen, producing an oxygen radical, which is much less reactive. These significantly slow down the rate of propagation.

- **Chain Transfer:** Contrary to the other mode of termination, chain transfer results in the distribution of only one radical but also the creation of another radical. Often, however, this newly created radical is not capable of further propagation and the most obvious effect of chain transfer is a decrease in the polymer chain length. If the rate of termination is much larger than the rate of propagation, then the very small polymers are formed with chain lengths of 2-5 repeating units. There are several types of chain transfer mechanisms.[13]

1. Chain transfer to solvent occurs when a hydrogen atom is abstracted from a solvent molecule, resulting in the formation of radical on the solvent molecules, which will not propagate further.
2. Chain transfer to monomer occurs when a hydrogen atom is abstracted from a monomer. While this does create a radical on the affected monomer, resonance stability of this radical discourages further propagation.
3. Chain transfer to initiator occurs when a polymer chain reacts with an initiator, which terminates that polymer chain, but creates radical initiators. This initiator can them begin new polymer chains. Therefore, contrary to the other forms of chain transfer, chain transfer to the initiator does allow for further propagation. Peroxide initiators are especially sensitive to chain transfer.
4. Chain transfer to polymer occurs when the radical of a polymer chain abstracts a hydrogen atom from somewhere on another polymer chain. This terminates one of the polymer chains, but allows the other to branch. When this occurs, the average molar mass remains relatively unaffected.

The simplified equations for the different mechanisms in a classical free radical polymerization are present in Table 2.

**Table 2:** Simplified equations for the different mechanisms in FRP.

| Equation | Mechanism |
|---|---|
|  | Initiation |
|  | Propagation |
| $RM_n^{\cdot} + RM_m^{\cdot}$ | Termination |

#### 2.2.1.2 Kinetics:

The reaction rates of the initiation, propagation, and termination can be described as follow.

$$v_i = \frac{d[RM_1^{\cdot}]}{dt} = 2k_d f[I] \qquad (1)$$

$$v_p = k_p[M][RM_n^{\cdot}] \qquad (2)$$

$$v_t = \frac{-d[RM_n^{\cdot}]}{dt} = 2k_t[RM_n^{\cdot}]^2 \qquad (3)$$

Under the steady state approximation, the concentration of active chain can be derived and expressed in terms of the other known species in the system.

$$[M^{\cdot}] = \left(\frac{k_d[I]f}{k_t}\right)^{1/2} \qquad (4)$$

### 2.2.2 Emulsion Polymerization:

Emulsion polymerization is used in the production of a wide range of specialty polymers including adhesives, paints, binders for nonwoven fabrics, additives for paper, etc.[14] Emulsion polymerization is the most promising technique to synthesize "green-polymers", especially if the monomer comes from a renewable resource because of the low impact of the process in the environment.

The term emulsion polymerization encompasses several processes: conventional emulsion polymerization, inverse emulsion polymerization, miniemulsion polymerization, dispersion polymerization and microemulsion polymerization, but the conventional emulsion polymerization accounts for the majority of the word's production ( $> 20 \times 10^6$ tones/year).[14]

Emulsion polymers are "products by process" whose main properties are determined during the polymerization; the critical point is to know how these process variables affect the final properties of the product. A possibility is to consider the

reactor as a black box and to develop empirical relationships between process variables and product properties.[14]

The fundamental mechanism of emulsion polymerization is illustrated in Figure 5. This is a type of radical polymerization that usually starts with an emulsion incorporating for water, monomer and surfactant, in conventional emulsion polymerization we have an oil in water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactant) in a continuous phase of water. The reaction of polymerization occurs in the latex particles that form spontaneously in the first few minutes of the process. Typically the latex particles have 100 nm in size, and are made of many individual polymer chains. [9]

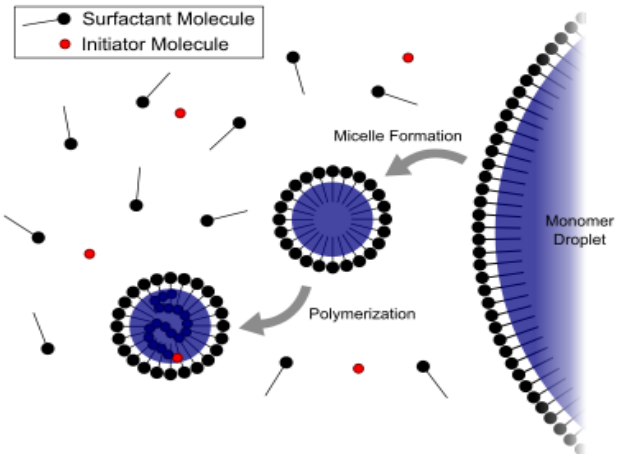



**Figure 5:** Scheme representative of emulsion polymerization.

The first successful theory to explain the distinct features of emulsion polymerization was largely developed by Smith and Ewart, and Harkins in the 1940s. Smith and Ewart arbitrarily divided the mechanism of emulsion polymerization into three stages or intervals.[15,16]

The Smith-Ewart-Harkins theory for the mechanism of free-radical emulsion polymerization is summarized by the following steps:

- A monomer is dispersed or emulsified in a solution of surfactant and water forming relatively large droplets of monomer in water.
- Excess surfactant creates micelles in the water.

- Small amounts of monomer diffuse through the water to the micelle.
- A water-soluble initiator is introduced into the water phase where it reacts with monomer in the micelles. This is considered **Smith-Ewart Interval 1**.
- The total surface area of the micelles is much greater than the total surface area of the fewer, larger monomer droplets; therefore the initiator typically reacts in the micelle and not the monomer droplet.
- Monomer in the micelle quickly polymerizes and the growing chain terminates. At this point the monomer-swollen micelle has turned into a polymer particle. When both monomer droplets and polymer particles are present in the system, this is considered **Smith-Ewart Interval 2**.
- More monomer from the droplets diffuses to the growing particle, where more initiators will eventually react.
- Eventually the free monomer droplets disappear and all remaining monomer is located in the particles. This is considered **Smith-Ewart Interval 3**.
- Depending on the particular product and monomer, additional monomer and initiator may be continuously and slowly added to maintain their levels in the system as the particles grow.
- The final product is a dispersion of polymer particles in water. It can also be known as a polymer colloid, a latex, or commonly and inaccurately as an 'emulsion'.

Smith-Ewart theory does not predict the specific polymerization behavior when the monomer is somewhat water-soluble. In these cases homogeneous nucleation occurs that the particles are formed without the presence or need for surfactant micelles.[9]

In case of vegetable oils and fatty acids, this kind of monomers have a high hydrophobicity, and the conventional emulsion polymerization would be limited by diffusion of monomer though water phase. Miniemulsion polymerization has been widely used to overcome this disadvantage, where homogeneous and stable monomer droplets are generated.[17]

### 2.2.3 Miniemulsion Polymerization:

A miniemulsion is a special case of emulsion. A miniemulsion is obtained by shearing a mixture comprising two immiscible liquid phases, one or more surfactants and, possibly, one or more co-surfactants to protect droplets against both diffusional degradation and droplet coagulation.[18]

There is a fundamental difference between traditional emulsion polymerization and a miniemulsion polymerization. Particle formation in the former is a mixture of micellar and homogenous nucleation; particles formed via miniemulsion however are mainly formed by droplet nucleation.[18]

In general the theory about the miniemulsion polymerization, consists of:

- A monomer is dispersed in an aqueous solution of surfactant; at this time the droplets in the system have a relative stability (droplet size around 50 to 500 nm).
- During the dispersion formation is necessary a high stirring mechanism, in order to achieve a steady state between the rate of coalescing and breaking in the droplets.
- Finally the polymerization is started by means of an initiator system (most often soluble in water), the droplets formed in the previous step are nucleated and polymerized without changing their characteristics.

Figure 6 represents an illustration of the different steps present in a miniemulsion polymerization.

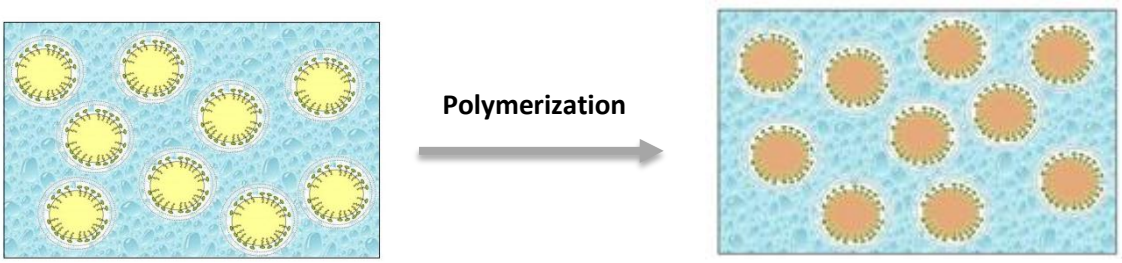



**Figure 6:** Scheme representative of miniemulsion polymerization.

# Chapter 3

## 3.1 Experimental Section:

In the experimental part of this project two processes were performed, for synthetize adhesives from incorporation of carboxylic acid groups, present in the composition of the vegetable oils.

### 3.1.1 Synthesis of Covalent Incorporation of Carboxylic Acids:

- **Synthesis of the Monomer:**

Figure 7 presents a scheme of the reaction that functionalizes the monomer by covalent incorporation of carboxylic acids.

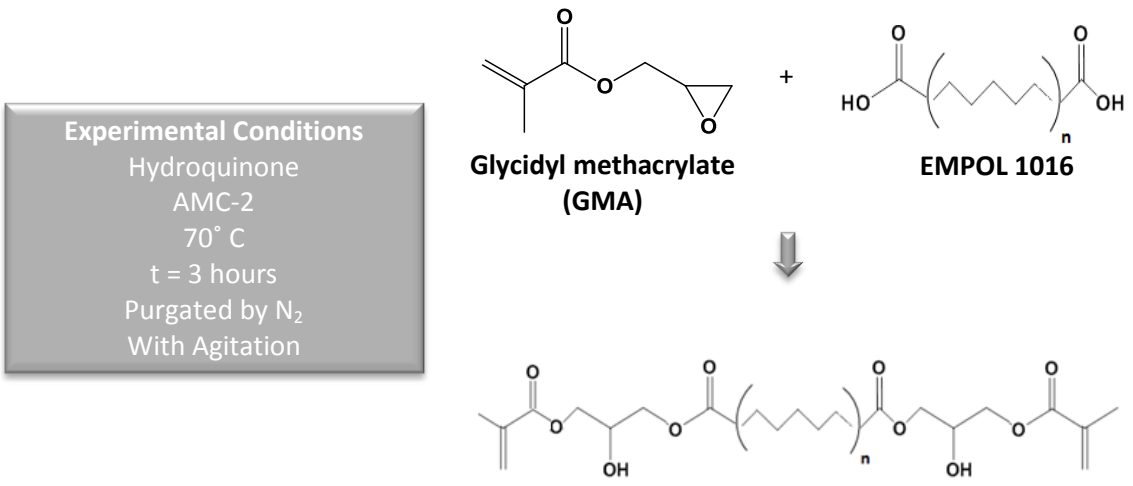



**Figure 7:** Illustration of the reaction that functionalizes the monomer by covalent incorporation of carboxylic acids.

✓ **Materials and Methods:**

EMPOL 1016 was purchased by Cognis, Glycidyl methacrylate (GMA) (purity ≥97%) was purchased by Sigma Aldrich, Hydroquinone was purchased by Riedel-de Haën, AMC-2 catalyst was kindly supplied by Aerojet Chemicals. For the determination of the acid number were used ethanolic solution of potassium hydroxide was purchased by Riedel-de Haën and phenolphthalein was purchased by Sigma-Aldrich and deuterated chloroform ($CDCl_3$) purchased by Cortecnet to $^1$H-NMR analysis. All Chemicals were used as received, without purification.

✓ **Procedure for the Synthesis of the Monomer:**

In a typical reaction of EMPOL1016-GMA, a stoichiometric mixture by weight of EMPOL 1016 and GMA was charged to the reactor together with hydroquinone (0.1 % in respect to the weight of the monomer) and AMC-2 catalyst (0.4% in respect to the weight of the monomer), which is a mixture of 50% trivalent organic chromium complexes and 50% phthalate esters,[19] was used. The reaction had been purged with nitrogen, and the system was heated at 70˚C using a silicon oil bath. The reaction occurs during 3 hours by constant agitation. This approach was done by following the procedure described by J. J. Scala et al.[20] Figure 8 presents the experimental setup used to carry out this synthesis. The different formulations used in this synthesis, are presented in Table 3.

**Figure 8:** Experimental setup used for the synthesis of covalent monomer.

**Table 3:** Formulations employed in the synthesis of the covalent monomers.

| Name of the Monomer | Weight Ratio EMPOL1016:GMA |
|---|---|
| EGMA1 | 2:1 |
| EGMA2 | 1:1 |
| EGMA3 | 1:2 |
| EGMA4 | 1:1.75 |
| EGMA6 | 1:1.5 |

- ✓ **Monomer Characterization:**

For the calculation of the acid number, titration was used to measure the amount of free acids groups in the system. The value of neutralization point was measured from a solution of 1g of synthesized monomer dissolved in 10 g of a mixture of ethyl acetate/ethanol (3/1, volume) and approximately 1mL of 1wt% phenolphthalein in ethanol. The solution was then titrated with ethanolic potassium hydroxide solution remained slightly pink colour for 30 seconds. Figure 9 illustrates the change of the colour of the titration solution for color pink.

**Figure 9:** Illustration of the change of the colour in the titration solution for the determination of the acid number.

To determine the functionalization degree of EMPOL 1016 and characterization of the monomer, small amounts of reaction solution were extracted at different intervals of time and analyzed by $^{1}H$ NMR spectroscopy. A Bruker DRX-500 spectrometer, 500 MHz was used and the samples were dissolved in deuterated chloroform. Figure 10 shows the generic chemical structure of the covalent monomers and Figure 11 illustrates the $^{1}H$ NMR spectra's of them (polymerization time = 0 min).

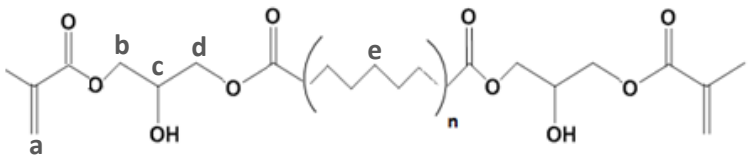



**Figure 10:** Chemical structure of the covalent monomers.

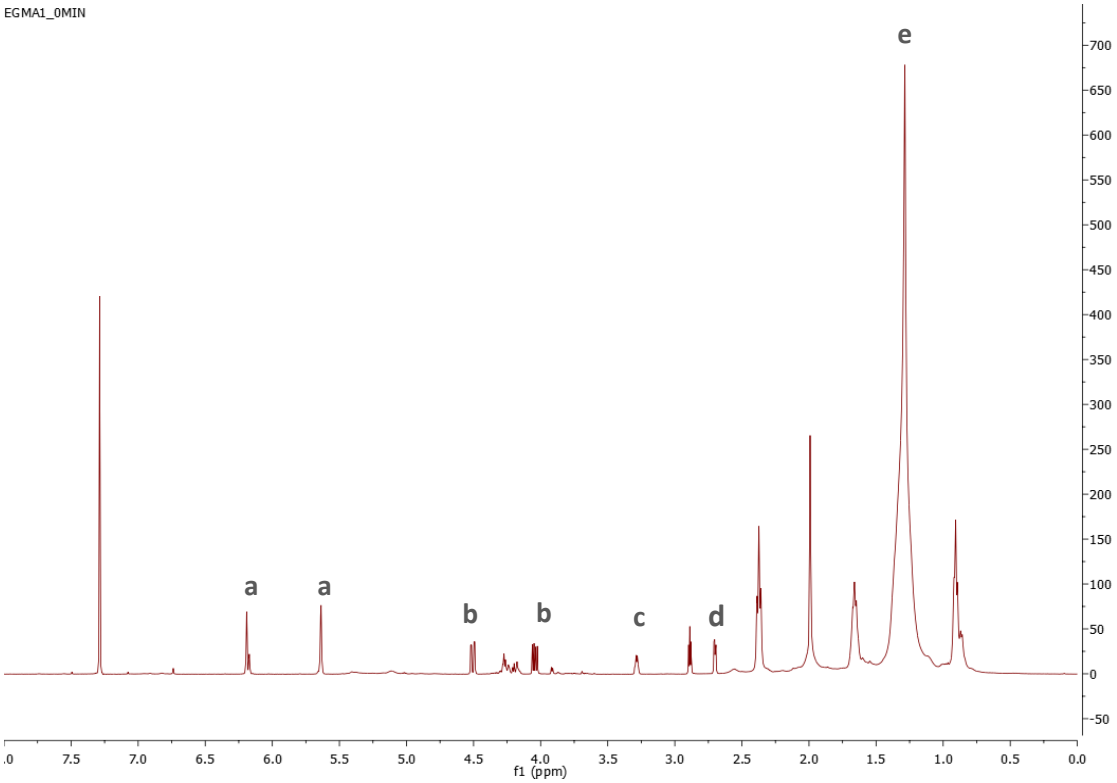



**Figure 11:** Illustration of $^{1}H$ NMR spectra, of the covalent monomer not functionalized (t = 0 min).

- **Miniemulsion Polymerization of the Monomer Synthesized:**

  - ✓ **Materials and Methods:**

The monomer used in this part of the work was synthesized and characterized using the methods described in topic 1 (Chapter 3) referent to the covalent incorporation of di carboxylic acids. Potassium persulfate (KPS) (purity 99%), tert-butyl hydroperoxide (TBHP) (70 wt. in $H_2O$), were supplied by Sigma-Aldrich and Ascorbic acid (ASA) (purity 99%), was purchased to Panreac and were used as initiators. The emulsifier used was alkyldiphenil oxide disulfonate (Dowfax 2A1 (anionic)) (45 wt% aqueous solution) which was purchased by Dow Chemicals Company. All Chemicals were used as received, without purification. Distilled water was used throughout all the work. 1,3,5-Bencenetricarboxilic acid (BTC) (internal reference) was purchased by Sigma-Aldrich and deuterated oxide ($D_2O$) was purchased by Cortecnet, which were used for the $^1H$ NMR analysis.

  - ✓ **Preparation of the Miniemulsion:**

In this part of the work, to obtain small and homogeneously distributed droplet size, the homogenization was carried out using two devices in serie: a sonicator and a high pressure homogenizer. Figures 12 and 13 illustrate a typical sonicator and high pressure homogenizer, respectively, present in our lab.

Miniemulsions were obtained from different wt% of solid contents, and different percentages of surfactante dispersed in water phase. To produce the miniemulsions, the organic and the aqueous phases were mixed by magnetic stirring (15 minutes at 700 rpm), and the resulted mixture was sonicated with a Branson 450 equipment (15 minutes and 80% duty cycle) under ice cooling. Finally, the

miniemulsion was further treated with a high-pressure homogenizer serie Niro-Soavi, NS1001L PANDA using 60.0 MPa in the first valve and 6.0 MPa in the second stage valve.

**Figure 12:** Illustration of a typical sonicator Branson 450.

**Figure 13:** Illustration of a typical homogenizer serie Niro-Soavi, NS1001L PANDA.

- ✓ **Miniemulsion Stability Measurement:**

The stability of the miniemulsions was assessed employing the Turbiscan LAB$^{expert}$. The working principle of the equipment is measuring the light that is transmitted and backscattered from a dispersion that is contained in a glass vial. Previous research works have shown the ability of the equipment for evaluating the stability of the dispersions. [21] For very stable miniemulsions, the backscattering data show minimum variation with time, because monomer droplets are not growing as consequence of coalescence or monomer diffusion. The technique results very attractive since it is possible to detect in an early stage, phenomena like creaming, sedimentation and coalescence. All the measurements were carried out at 30˚C for six hours. Figure 14 illustrates a Turbiscan LAB$^{expert}$.

**Figure 14:** Illustration of a typical Turbiscan LAB$^{expert}$.

- ✓ **Miniemulsion Polymerization:**

In this part of this work different formulations of latexes were synthetized by batch and semi-continuous miniemulsion polymerization. In Table 4 the different formulations are presented for the miniemulsions performed.

**Table 4:** Different miniemulsions formulations employed.

| Polymer Name | Monomer | % Solid Contents (SC) | Type of Initiator | % Initiator | Type of Emulsifier | % Emulsifier |
|---|---|---|---|---|---|---|
| PEGMA1 | EGMA4 | 30 | KPS | 1 | Dowfax 2A1 | 1 |
| PEGMA2 | EGMA2 | 30 | KPS | 1 | Dowfax 2A1 | 1 |
| PEGMA3 | EGMA4 | 10 | KPS | 1 | Dowfax 2A1 | 2 |
| PEGMA4 | EGMA6 | 20 | TBHP-ASA | 1 | Dowfax 2A1 | 2 |
| PEGMA5 | EGMA6 | 20 | KPS | 1 | Dowfax 2A1 | 2 |
| PEGMA6 | EGMA1 | 20 | KPS | 1 | Dowfax 2A1 | 2 |
| PEGMA7 | EGMA1 | 20 | KPS | 1 | Dowfax 2A1 | 2 |
| PEGMA8 | EGMA6 | 20 | TBHP-ASA | 1 | Dowfax 2A1 | 2 |
| PEGMA9 | EGMA6 | 20 | KPS | 1 | Dowfax 2A1 | 2 |
| PEGMA10 | EGMA6 | 20 | KPS | 1 | Dowfax 2A1 | 2 |
| PEGMA11 | EGMA6 | 20 | KPS | 2 | Dowfax 2A1 | 5 |
| PEGMA12 | EGMA2 | 20 | KPS | 1.5 | Dowfax 2A1 | 2 |

The formulations presented in Table 4 were performed in distinct types of reactors with different types of agitators, but the majority of them were carried out in a reactor equipped with a jacket, reflux condenser, stirred, sampling device and nitrogen inlet.

The latexes were synthesized by following the miniemulsion recipe shown in Table 4. The miniemulsion was added to the reactor and kept under stirring and nitrogen atmosphere. For batch polymerization the thermal initiator KPS was added into the reactor as a shot when the reaction temperature was reached (70˚C) and the reaction was running for 4 hours. In semi-continuous polymerizations when redox initiator are used TBHP-ASA (%wt (TBHP:ASA)=2/1), the reductant (ASA) was injected

as a shot when the reaction mixture reached the desired temperature (70˚C) and the oxidant (TBHP) was feed continuously into the reaction for 4 hours. Samples were withdrawn at regular intervals and the polymerization was short-stopped with hydroquinone.

- ✓ **Polymer Characterization:**

For the characterization of the polymer the conversion was calculated by previous following the depletion of the signals in $^{1}$H NMR spectra of the monomer. For the preparation of the samples, they were dissolved in BTC (Internal reference) and distilled water.

The conversion degree during the polymerization time was calculated using the following formula:

$$Conversion_{generic\ time} = 1 - \frac{\left( {}^{A_{Abs,Poly}}/_{A_{Abs,Mon}} \right)_{generic\ time}}{\left( {}^{A_{Abs,Poly}}/_{A_{Abs,Mon}} \right)_{t=0}} \qquad (5)$$

To perform the previous calculation, it was necessary to select two pick's, in NMR spectra, one of them referent to the polymer and another one, fix during the polymerization time, referent to the monomer. Comparing the depletion of the polymer pick in relation to the monomer pick, during the time of the reaction, it is possible to calculate the conversion degree. Wherein $A_{Abs}$, corresponds the absolute area of the pick considered.

### 3.1.2 Synthesis of Ionic Incorporation of Carboxylic Acids:

- **Synthesis of the Monomer:**

Figure 15 presents a scheme of the reaction for synthesizing monomers from ionic incorporation of carboxylic acids.

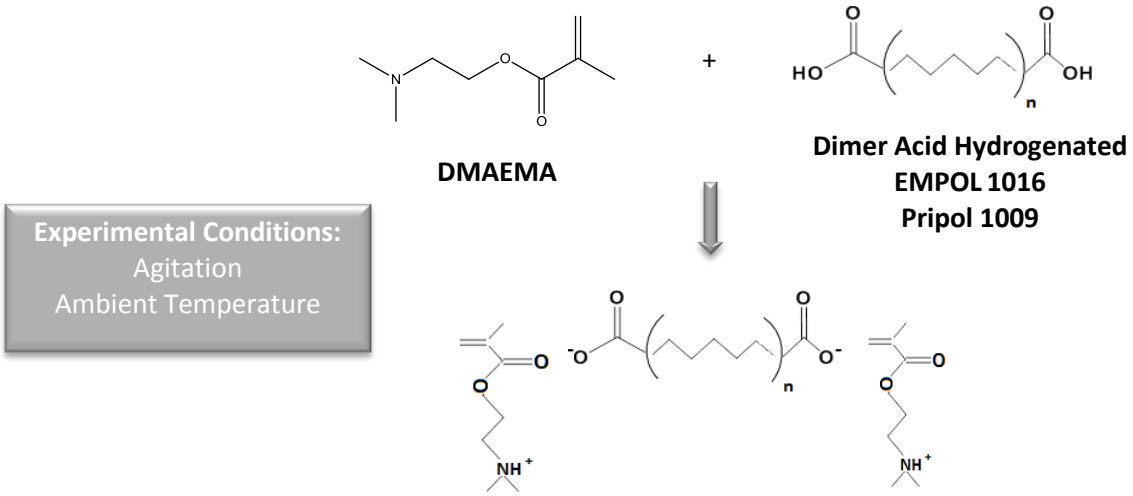



**Figure 15:** Illustration of the reaction for synthesizing monomers from ionic incorporation of carboxylic groups.

- ✓ **Materials and Methods:**

EMPOL 1016 was purchased by Cognis, Pripol 1009, Pripol 1040 were purchased by CRODA, Dimer Acid hydrogenated, Sunflower seed oil, Dodecanedioic acid, 2-(dimethylamino) ethyl methacrylate (DMAEMA) and 2-(dimethylamino)ethyl acrylate (DMAEA) were purchased by Sigma-Aldrich. All Chemicals were used as received, without purification. For $^{1}H$ NMR and $^{13}C$ NMR measurements the samples were dissolved in deuterated $CDCl_3$ that was purchased to Sigma-Aldrich.

✓ **Procedure for the Synthesis of the Monomer:**

In a typical reaction, a stoichiometric mixture of one generic di carboxylic acid and DMAEMA were simultaneously added in a glass under vigorous stirring without nitrogen atmosphere. The proton transfer reaction was carried out for 30 minutes and the obtained 2-(dimethylamino) ethyl methacrylate – generic dimer acid protic ionic liquid was characterized. The same syntheses with 2-(dimethylamino) was also carried out with ethyl acrylate (DMAEA). The different formulations for the synthesis of monomers performed are presented in Table 5.

**Table 5:** Formulations employed in the synthesis of the ionic monomers.

| **Synthesis of monomer with DMAEMA** | |
|---|---|
| **Type of acid** | **Weight Ratio Acid : DMAEMA** |
| EMPOL1016 | 1:1 |
| EMPOL1016 | 2:1 |
| EMPOL1016 | 3:1 |
| Dimer Acid Hydrogenated | 1:1 |
| Dimer Acid Hydrogenated | 1.5:1 |
| Dimer Acid Hydrogenated | 1.75:1 |
| Dimer Acid Hydrogenated | 2:1 |
| Dimer Acid Hydrogenated | 2.25:1 |
| Dimer Acid Hydrogenated | 2.5:1 |
| Dimer Acid Hydrogenated | 3:1 |
| Dimer Acid Hydrogenated | 4:1 |
| Pripol 1040 | 2:1 |
| Pripol 1040 | 1.7:1 |
| Pripol 1009 | 1.75:1 |
| Pripol 1009 | 2:1 |
| Sunflower seed oil | 1.75:1 |
| Dodecanedioic acid | 1:2 (Molar ratio) |
| **Synthesis of monomer with DMAEA** | |
| **Type of acid** | **Weight Ratio Acid : DMAEA** |
| Dimer Acid Hydrogenated | 2:1 (Molar ratio) |
| Dimer Acid Hydrogenated | 2:1 |

✓ **Monomer Characterization:**

For the characterization of the monomer obtained, small amount of reaction solution were extracted and analyzed by $^{1}H$ NMR, $^{13}C$ NMR and infra-red spectroscopy (FTIR). The samples for NMR measurements were dissolved in deuterated chloroform. Figure 16 shows the chemical structure of the monomer. Figure 17 represents a $^{1}H$ NMR spectra's of them. The composition of the monomer in the illustration is a mixture of Dimer Acid hydrogenated and 2-(dimethylanino) ethyl methacrylate with a weight ratio 2:1.

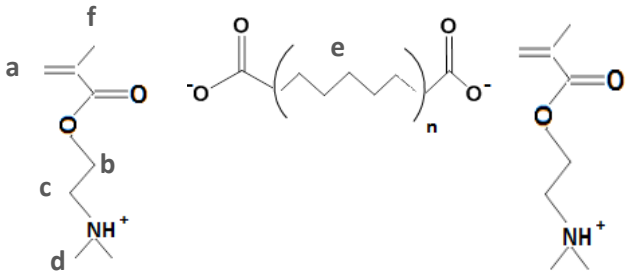



**Figure 16:** Chemical structure of the ionic monomers.

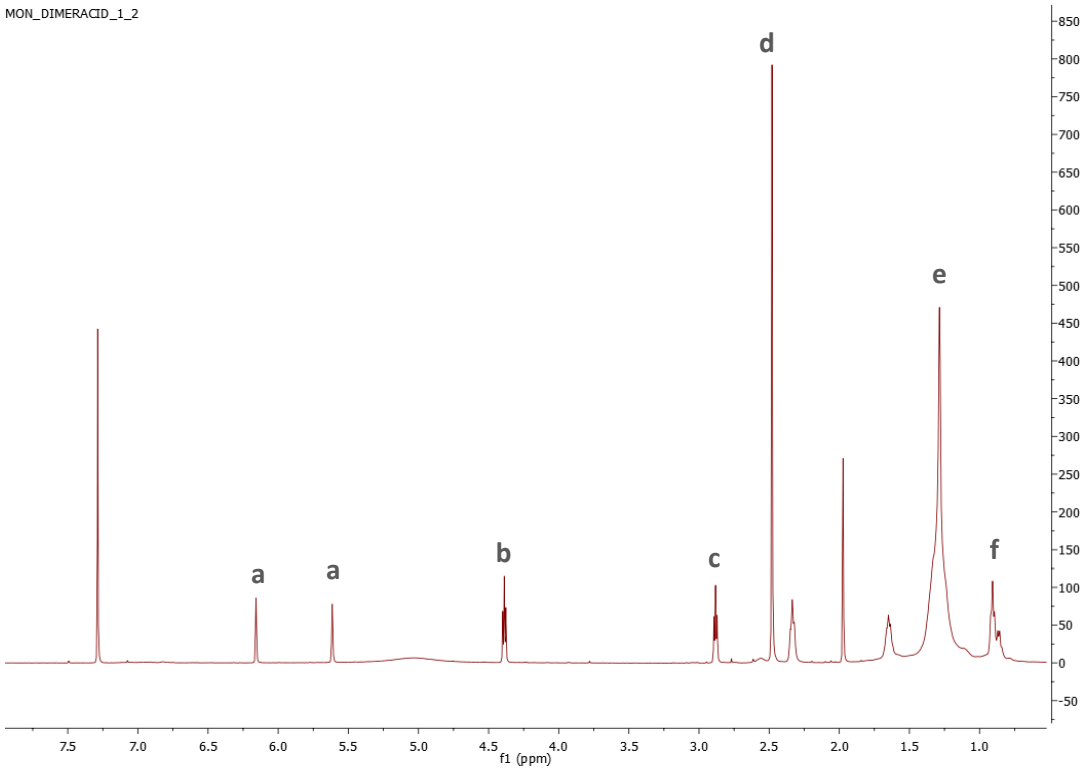



**Figure 17:** Representation of $^{1}H$ NMR spectra's of the ionic monomer.

- **Polymerization of the Monomer Synthesized:**

✓ **Materials and Methods:**

The monomers obtained before by ionic incorporation of di carboxylic acids were polymerized in this part of the work. AIBA (purity 97%) purchased to Sigma Aldrich, was used as initiator. The emulsifiers used were alkyldiphenil oxide disulfonate (Dowfax 2A1 (anionic)) (45 wt% aqueous solution) was purchased by Dow Chemicals Company and Disponil 1080 (no ionic) (80 wt% aqueous solution) was purchased by Cognis. All Chemicals were used as received, without purification. Distilled water was used throughout all the work. For $^{1}H$ NMR measurements the samples were dried and dissolved in Methanol and Chloroform deuterated was purchased by Sigma-Aldrich.

✓ **Free Radical Polymerization of Protic Ionic Liquids Monomers:**

The monomer was polymerized using conventional emulsion polymerization. Emulsions with different wt% of solid contents were carried out. Typically, to a 50 mL glass reactor, monomer, emulsifier, AIBA and distilled water were charged. The reactor was purged with $N_2$ for 30 minutes and then immersed in an oil bath at 70˚C for 24 hours. Table 6 presents the different formulations used for the polymerizations carried out in this part of the project.

**Table 6:** Different emulsions formulations employed.

| **Synthesis with EMPOL 1016** | | | | | |
|---|---|---|---|---|---|
| **Polymer Name** | **Weight Ratio EMPOL:DMAEMA** | **% SC** | **Type of Emulsifier** | **% Emulsifier** | **% Initiator** |
| 1st Experience | 1:1 | 25 | Dowfax 2A1 | 3 | 1 |
| PEDMAEMA1 | 2:1 | 8 | Dowfax 2A1 | 7 | 1 |
| PEDMAEMA2 | 2:1 | 16 | Dowfax 2A1 | 4 | 1 |
| PEDMAEMA3 | 3:1 | 10 | Dowfax2A1 | 0 | 1 |
| PEDMAEMA4 | 3:1 | 13 | Dowfax2A1 | 2 | 1 |
| PEDMAEMA5 | 2:1 | 16 | Dowfax2A1 | 2 | 1 |
| PEDMAEMA6 | 2:1 | 9 | Disponil1080 | 4 | 1 |
| PEDMAEMA7 | 2:1 | 15 | Disponil1080 | 4 | 1 |

| | | | | | |
|---|---|---|---|---|---|
| PEDMAEMA8 | 2:1 | 17 | Disponil1080 | 4 | 1 |
| PEDMAEMA9 | 1:1 | 11 | Disponil1080 | 4 | 1 |
| **Synthesis with Dimer Acid Hydrogenated** | | | | | |
| **Polymer Name** | **Weight Ratio Dimer Acid:DMAEMA** | **% SC** | **Type of Emulsifier** | **% Emulsifier** | **% initiator** |
| PDADMAEMA1 | 1:1 | 5 | Disponil1080 | 4 | 1 |
| PDADMAEMA2 | 2:1 | 15 | Disponil1080 | 4 | 1 |
| PDADMAEMA3 | 2:1 | 5 | Disponil1080 | 4 | 1 |
| PDADMAEMA4 | 2:1 | 10 | Disponil1080 | 4 | 1 |
| PDADMAEMA5 | 3:1 | 15 | Disponil1080 | 4 | 1 |
| PDADMAEMA6 | 4:1 | 15 | Disponil1080 | 4 | 1 |
| PDADMAEMA7 | 1.5:1 | 15 | Disponil1080 | 4 | 1 |
| PDADMAEMA8 | 2.5:1 | 15 | Disponil1080 | 4 | 1 |
| PDADMAEMA9 | 1.75:1 | 10 | Disponil1080 | 4 | 1 |
| PDADMAEMA10 | 2.25:1 | 10 | Disponil1080 | 4 | 1 |
| PDADMAEMA11 | 1.75:1 | 15 | Disponil1080 | 4 | 1 |
| PDADMAEMA12 | 2.25:1 | 15 | Disponil1080 | 4 | 1 |
| **Polymer Name** | **Weight Ratio Dimer Acid:DMAEA** | **% SC** | **Type of Emulsifier** | **% Emulsifier** | **% Initiator** |
| PDADMAEA1 | 2:1 | 15 | Disponil1080 | 4 | 1 |
| PDADMAEA2 | 1:2 | 15 | Disponil1080 | 4 | 1 |
| **Synthesis with Pripol** | | | | | |
| **Polymer Name** | **Weight Ratio Pripol X : DMAEMA** | **% SC** | **Type of Emulsifier** | **% Emulsifier** | **% Initiator** |
| PPripol1040_1 | 2:1 | 15 | Disponil1080 | 4 | 1 |
| PPripol1040_2 | 1.68:1 | 15 | Disponil1080 | 4 | 1 |
| PPripol1009_1 | 2:1 | 15 | Disponil1080 | 4 | 1 |
| PPripol1009_1 | 1.75:1 | 15 | Disponil1080 | 4 | 1 |
| **Synthesis with Sunflower Seed Oil** | | | | | |
| **Polymer Name** | **Weight Ratio SFSOIL : DMAEMA** | **% SC** | **Type of Emulsifier** | **% Emulsifier** | **% Initiator** |
| PSFSOil_1 | 1.75:1 | 15 | Disponil1080 | 4 | 1 |
| **Synthesis Dodecanedioic Acid** | | | | | |
| **Polymer Name** | **Molar Ratio 12dioic:DMAEMA** | **% SC** | **Type of Emulsifier** | **% Emulsifier** | **% Initiator** |
| P12dioic_1 | 2:1 | 10 | Disponil1080 | 4 | 1 |

*Continuation of the Table 6

✓ **Characterization of the polymer:**

After the reaction the characterization of the polymer conversion is calculated using the equation (5) by previous following the depletion of the signals in $^{1}H$ NMR spectra of the monomer. For the preparation of the samples, these were dried and dissolved in $CDCl_3$ and methanol deuterated. In this part of the project, the characterization of the adhesive properties for the different types of polymers synthetized was done.

- **Adhesive Properties:**

The adhesive properties are characterized by an optimal balance of tack, peel resistance and shear strength properties. Tack is an adhesive property related to bond formation and to the instantaneous attraction of an adhesive to a substrate. Peel strength measure the ability of the adhesive to resist forced delamination and, finally, shear strength is related to the internal or cohesive strength of the adhesives.[22]

✓ **Loop Tack:**

For samples preparation, latex was first neutralized using acetone. Films were prepared using an electrosticaly discharged treated 29 µm thick polypropylene (PP) film as backing. Over this backing a 120 µm wet film was applied and dried first at 23˚C and 55% of humidity for approximately 30 minutes and heated at 60˚C for additional half and hour. The final dry film was around 50-60 µm thick. The samples were covered by silicon paper in order to handle them easier and finally were cut following standard dimensions (Figure 18).

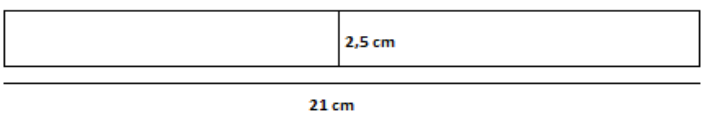



**Figure 18:** Dimensions of the samples prepared for the loop tack test.

For performing the experience, the coated was folded to form loop with the adhesive facing outwards. The ends of the loop were clamped for the distance of 10 nm into the top jaw of Instron equipment leaving the loop hanging vertically downwards. The loop was positioned in contact with the surface at a speed of 300 mm/min till the obtaining of full contact area (2,5 cm × 2,5 cm) and then, the direction of the machine was immediately reversed and the separation between the loop and the surface was carried out at 300 mm/min clam velocity. The value of the loop tack was the maximum value of the peak given by the equipment, averaged for four tests per latex. Figure 19 represents an illustration of loop tack test.

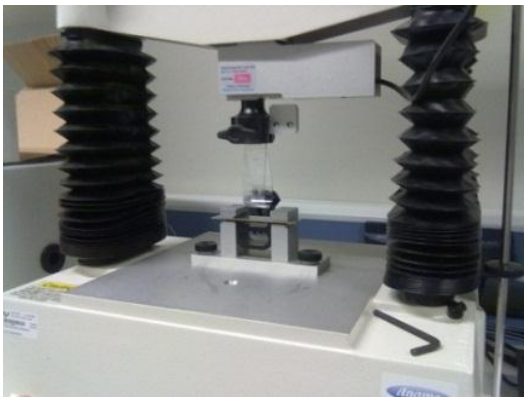


**Figure 19:** Illustration of loop tack experiment.

- ✓ **Probe Tack:**

In a typical probe tack test, a flat-ended probe comes in contact with an adhesive film cast in a glass substrate. For samples preparation, neutralized latexes were cast in a microscope glass by using a square applicator and dried for 48 hours at room temperature. The final thickness of the films was around 100 µm.

The glass slides were fixed in the upper place on a costume-designed apparatus developed at the ESPCI with the adhesive film facing down. The parallelism between the sample and the probe was assured by three independent motors that can level this plate. A cylindrical 5mm diameter stainless steel was used as probe. The displacement of the probe was measured with a LVTD extensometer. The experimental parameters used were: contact area 16,625 $mm^2$, product height 0,018 mm. To check the reproducibility, three to five experiments were performed for each latex and debonding velocity. The Figure 20 represents an illustration of probe tack experiment.


**Figure 20:** Illustration of probe tack test.

- ✓ **Peel Resistance:**

Peel resistance is a measure of the force required to peel away a strip of tape from a rigid surface at a specific angle and speed. In this work, the tests were performed using an 180˚ angle and a 300 mm/min speed in an Instron equipment. The measurements were carried out after 24 hours the adhesive was attached to the stainless steel testing substrate. Figure 21 represents an illustration of peel resistance experiment.

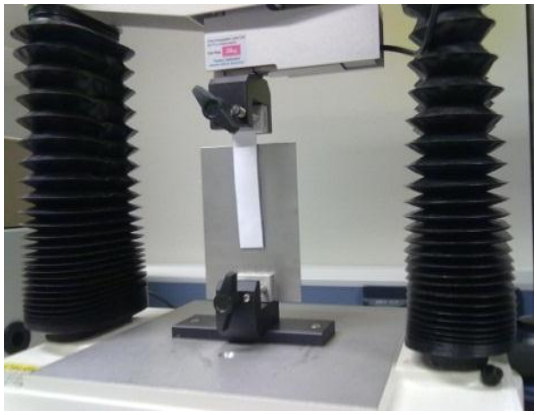


**Figure 21:** Illustration of peel resistance experiment.

For samples preparation, latexes were first neutralized using acetone. Films were prepared using an electrostatically discharged treated 29 µm thick polypropylene (PP) film as backing. Over this backing, a 120 µm wet film was applied and dried first at 23˚C and 55% of humidity for 30 minutes and heated at 60˚C for additional half and hour. The final dry film was around 50-60 µm. The samples were covered by silicon

paper in order to handle them easier and finally were cut following standard dimensions (Figure 22).

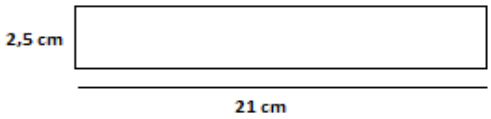



**Figure 22:** Dimensions of the samples prepared for the peel test.

The samples were then applied to a standard stainless panel using a given pressure (2 kg roller) to make the contact. The roller was passed 4 times. For performing the test, the free of the sample was doubled back, protected by paper, and clamped to the upper jaw of the Intron equipment. The adhesion value was the average peel force obtained during the peeling process. The final value was calculated as the average of 4 measurements per latex.

- ✓ **Shear Resistance and SAFT:**

The shear strength is the internal or cohesive strength of the adhesive. The shear resistance is the measurement carried out at a constant temperature while shear adhesion failure temperature (SAFT) refers to the upper temperature limit at which an adhesive is able to support a certain amount of weight.

The holding power shear test consist in applying under pressure a standard area of tape (2,5 cm × 2,5 cm) to a substrate and applying a standard weight (1 kg) until failure. The substrate where the adhesive is attached should be oriented 2 degrees from the vertical in order to assure that the tape will experience no peeling action only shear.

For samples preparation, latex was first neutralized using ammonia. Films were prepared using a 23 µm Polyester (PET) film as backing. Over this backing, a 120 µm wet film was applied and dried at 23 ˚C and 55% of humidity for 30 minutes and heated at 60˚C for additional half and hour. The final dry film was around 50-60 µm thick. The samples were covered by silicon paper in order to handle them easier and finally were cut following standard dimensions (Figure 23). Then the 2,5 cm × 2,5 cm

area was attached to the testing substrate. For the samples prepared for SAFT measurements, a high temperature resistance tape, a silicone polyester tape was further attached to the surface of the film in order to reinforce it.

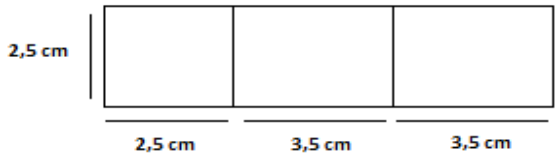



**Figure 23:** Dimensions of the samples prepared for shear and SAFT tests.

Tests were performed in a SAFT oven. The oven contain three metal panels were 12 samples can be clamped. Usually, 4 samples for each latex were tested in order to check the reproducibility of the adhesive occurred, the standard weights fall into a weight detector which stopped the counter of the corresponding sample. The oven was connected to a computer where the time and the temperature of failure were recorded. Shear resistance was measured over the films at 30˚C. Before starting the tests, the samples were allowed to be at 30˚C during 30 minutes. SAFT was measured using temperature ramp of 1˚C/min from 30˚C to 210 ˚C. In this case, before starting the tests, the samples were first kept at 30 ˚C for 24 hours. Figure 24 illustrates the initiation of the Shear and SAFT.

**Figure 24:** Illustration of the initiation of SAFT and Shear tests.

# Chapter 4

## 4.1 Experimental Results and Discussion:

### 4.1.1 Synthesis of Covalent Incorporation of Carboxylic Acids:

- **Synthesis of the Monomer:**

During the synthesis of the monomer it was investigated the evolution of the acid number (NA) and functionalization degree of EMPOL 1016 in the course of the polymerization time. Table 7 presents the final acid number measured for the different monomers synthesized and the functionalization degree for all of them.

**Table 7:** Results obtained in the different synthesis of the monomer's about the evolution of the acid number and functionalization degree during the polymerization time.

| Monomer Name | Weight Ratio EMPOL:GMA | Final Acid Number (mg KOH/ g amostra) | Functionalization Degree |
|---|---|---|---|
| EGMA1 | 2:1 | 92 | 100 |
| EGMA2 | 1:1 | 15 | 100 |
| EGMA3 | 1:2 | 8 | Epoxide groups free |
| EGMA4 | 1:1.75 | 8 | Epoxide groups free |
| EGMA6 | 1:1.5 | 4 | 99 |

Figure 25 illustrates the evolution of the acid number in the course of the polymerization time for monomer EGMA3. It should be noted that the sample at initial time (0 min) represented in the graph is only measured when the system reaches the temperature 70˚C.

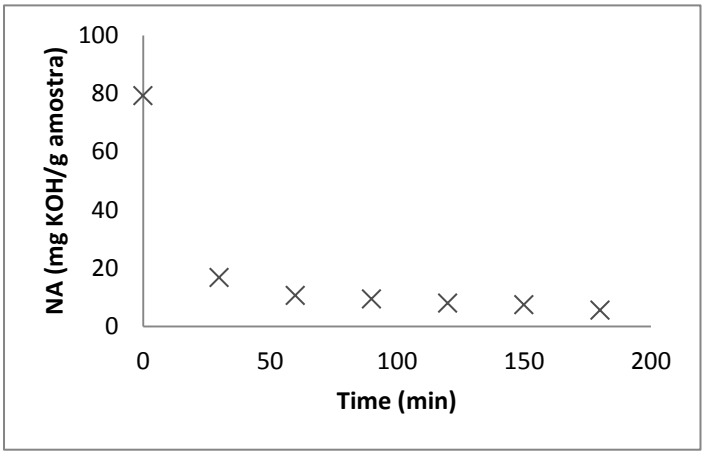



**Figure 25:** Evolution of the acid number during the polymerization time for monomer EGMA3.

Figure 26 shows the evolution of $^{1}H$ NMR spectra's during the polymerization time referent to the synthesis of the monomer EGMA2. Depletion of the protons at 4.5 and 4.0 ppm on 150 minutes confirms the absence of free monomer and therefore total monomer conversion.

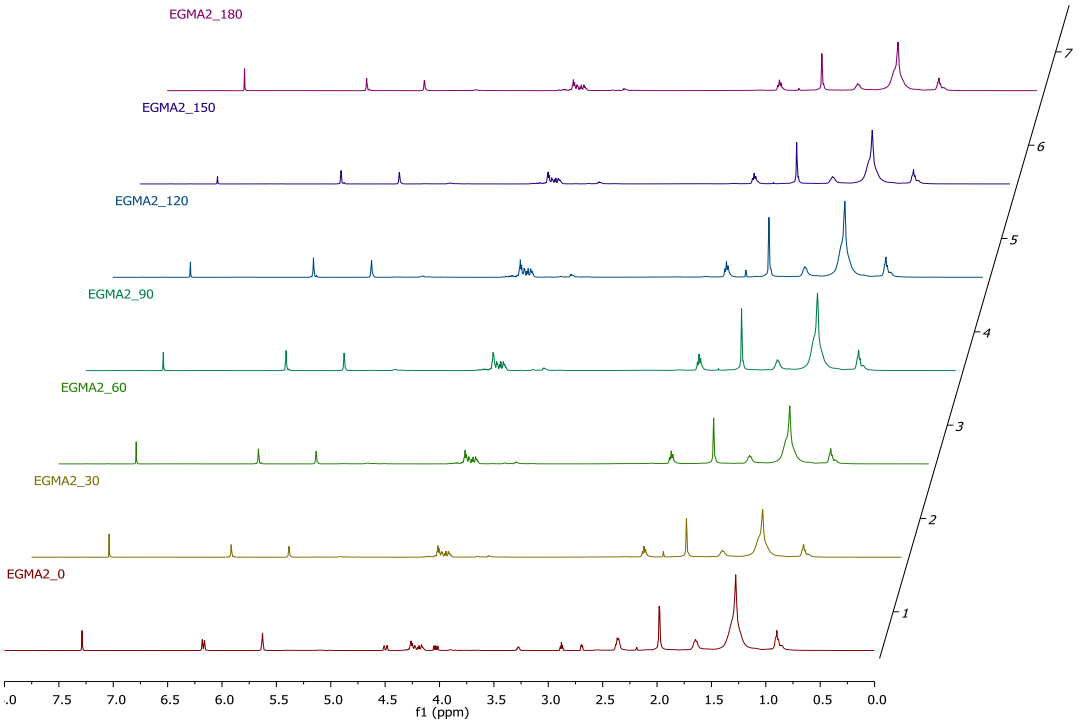



**Figure 26:** $^{1}H$ RMN spectra's of EGMA2 polymerization at different reaction times. 1) 0 minutes; 2) 30 minutes; 3) 60 minutes; 4) 90 minutes; 5) 120 minutes; 6) 150 minutes; 7) 180 minutes.

- ✓ **Preparation of the Miniemulsification:**

In a first attempt, the miniemulsification was prepared by ultrasonicating the pre-emulsion at 80 % amplitude under ice cooling. In order to achieve smaller and more homogeneously distributed droplets, the sonicated pre-emulsion was homogenized in a high pressure homogenizer. After the preparation of the miniemulsification, its stability was studied. Figure 27 shows the backscattering profile of the miniemulsion, prepared with the monomer EGMA1, during six hours of scanning. There is no change in backscattered light intensity, indicating that the miniemulsion is very stable.

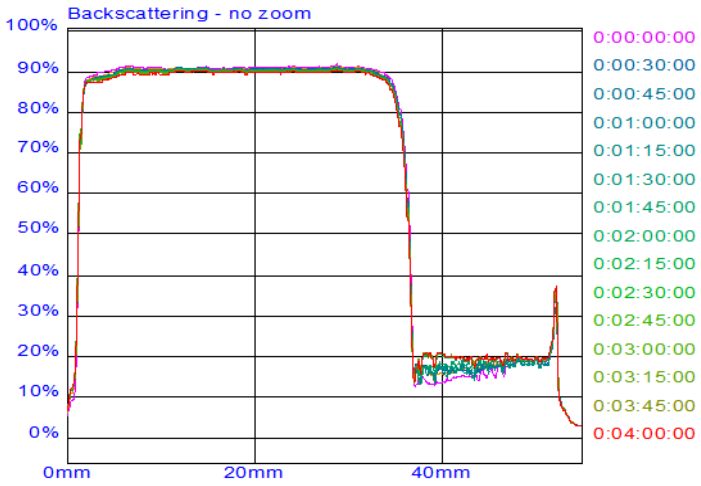



**Figure 27:** Stability of the miniemulsion prepared with monomer EGMA1 measured in a Turbiscan LAB$^{expert}$.

- **Miniemulsion Polymerization:**

After the preparation of the miniemulsion we proceeded to their polymerization. During miniemulsion polymerization the evolution of the conversion degree and the particle size ($d_p$) was investigated. Table 8 presents a summary of the results obtained.

**Table 8:** Summary of the polymerizations achieved by covalent monomers synthesizes.

| Polymer Name | Monomer Name | % SC | % Emulsifier | Type of Initiator | Conversion | $d_d$ (nm) | $d_p$ (nm) | % Coagulum |
|---|---|---|---|---|---|---|---|---|
| PEGMA1 | EGMA4 | 30 | 1 | KPS | - | - | - | 100 |
| PEGMA2 | EGMA2 | 30 | 1 | KPS | - | - | - | 100 |
| PEGMA3 | EGMA4 | 10 | 1 | KPS | 84 | 135 | 156 | 1 |
| PEGMA4 | EGMA6 | 20 | 2 | TBHP-ASA | 100 | 129 | 164 | 12 |
| PEGMA5 | EGMA6 | 20 | 2 | KPS | 100 | 143 | 153 | 25 |
| PEGMA6 | EGMA1 | 20 | 2 | KPS | 100 | 145 | 140 | 0 |
| PEGMA8 | EGMA1 | 20 | 2 | TBHP-ASA | 100 | 137 | 142 | 13 |
| PEGMA9 | EGMA6 | 20 | 2 | KPS | 94.76 | 128 | 145 | 13 |
| PEGMA10 | EGMA6 | 20 | 2 | KPS | 95.61 | 128 | 165 | 14 |
| PEGMA11 | EGMA6 | 20 | 5 | KPS | 100 | 112 | 110 | 13 |

In Figure 28 is presented the evolution of the conversion degree for PEGMA4 during the polymerization time, and Figure 29 presents the study about the evolution of the particle size for the same polymer.

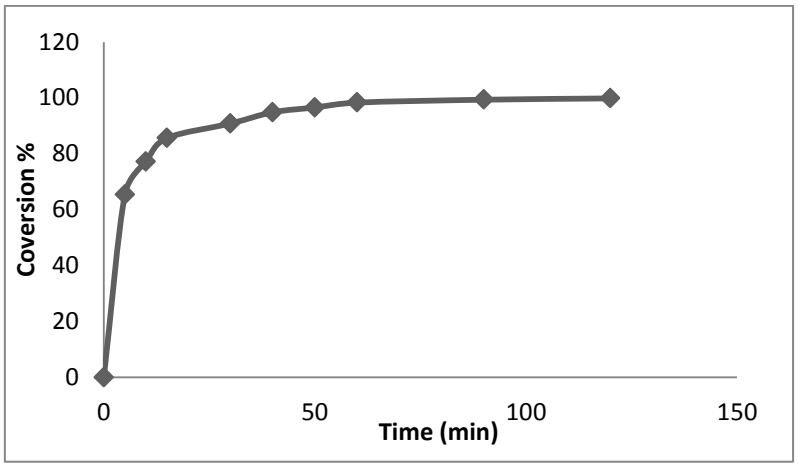



**Figure 28:** Evolution of the polymerization degree for PEGMA4 during the reaction time.

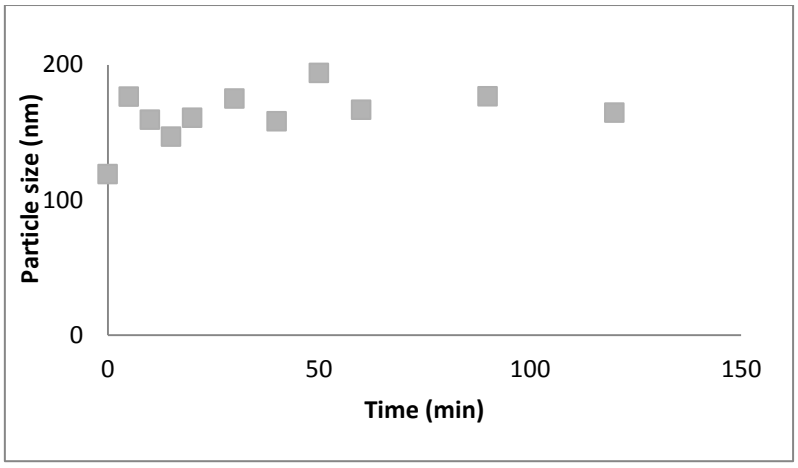



**Figure 29:** Evolution of the particle size for PEGMA4 during the reaction time.

For calculation of the conversion degree during the polymerization was used $^{1}H$ NMR analysis. The Figure 30 shows the evolution of the $^{1}H$ NMR spectra's during the polymerization time using the monomer EGMA6 synthesized with 20 % of solid contents, in respect to the total weight, and TBHP-ASA initiator (PEGMA4). Depletion of the signals of protons at 6.1 and 5.7 ppm on 60 minutes confirms the absence of

free monomer and therefore total conversion. Similar results were obtained when KPS was used as initiator, but the kinetic of the reaction occurs more slowly with KPS initiator than TBHP-ASA. In terms of initiators efficiency, there are no significant differences, because generally all polymerizations were successfully carried out leading to total conversions. The evolution of the particle size during the polymerization time maintains generally a constant diameter along of the reaction time, indicating that the miniemulsion was stable. On the other hand, in all of experiments realized with this system, occurs a little coagulum formation, this fact is difficult to explain because different reactions at different conditions occurred and in majority of them occurs some coagulum formation. After film formation all of them didn't have good adhesives properties. About the physic aspect of the films obtained all of them are very rigid and broken easily when subjected to pressure (Figure 31). This perception can be explained by the fact that the final product may be exceptionally reticulated.

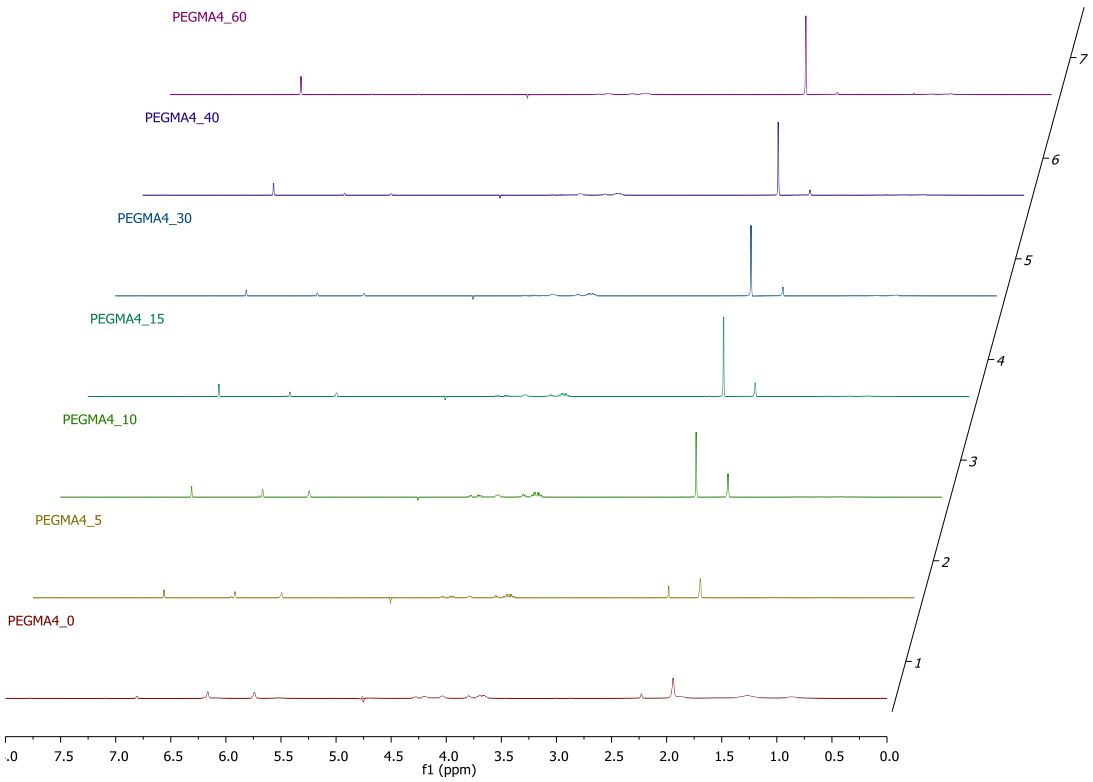



**Figure 30:** $^{1}$H RMN spectra of EGMA polymerization at different reaction times. 1) 0minutes; 2) 5minutes; 3) 10 minutes; 4) 15 minutes; 5) 30 minutes; 6) 40 minutes; 7) 60 minutes.

**Figure 31:** Final film obtained after drying and subject to pressure.

### 4.1.2 Synthesis of Ionic Incorporation of Carboxylic Acids:

- **Synthesis of the Monomer:**

During the synthesis of the monomer the conversion of the pick's from carboxylic group to carboxylate was analyzed over the time by FTIR spectroscopy, $^{1}H$ RMN and $^{13}C$ NMR. Figure 32, 33 and 34 show respectively the conversion of the carboxylic group in carboxylate from the different analysis realized at different times. The changes on the picks between 5 minutes and 1 hour are not significant relatively to the results after 24 hours, this explain that variations occur in the structure of the monomer during the time for the ionic change, until a stable structure is obtained.

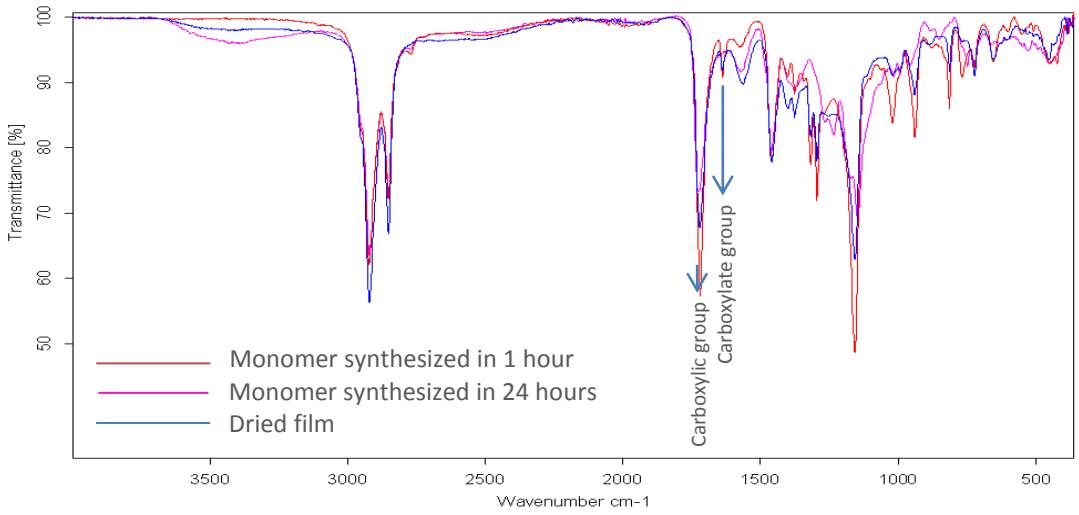



**Figure 32:** Analysis about the conversion of carboxylic group in carboxylate over the time in FTIR spectra.

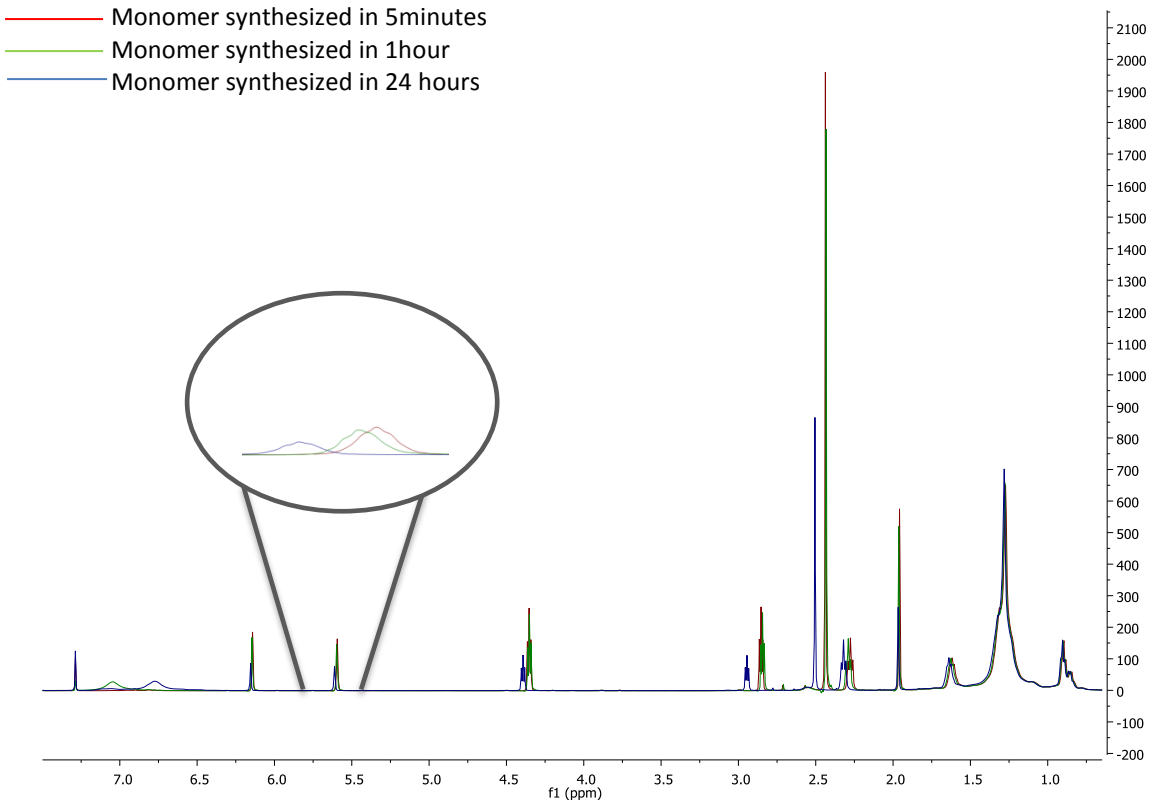



**Figure 33:** Analysis about the conversion of carboxylic group in carboxylate over the time in $^{1}$H NMR spectra.

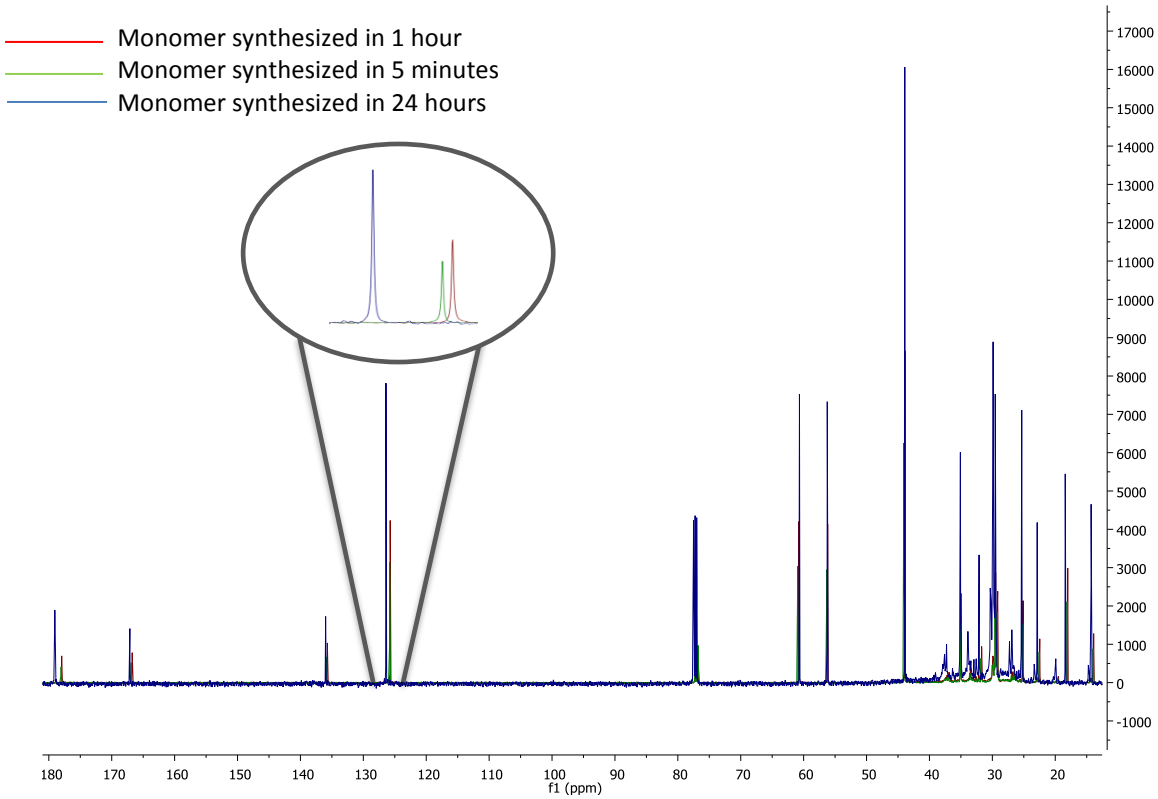



**Figure 34:** Analysis about the conversion of carboxylic group in carboxylate over the time in $^{13}$C NMR spectra.

- **Characterization of Adhesives Properties and Kinetic of the Polymerizations:**

In Table 6 (Chapter 3) are show the different types of synthesis learned during the experimental part of this work. After performing the polymerizations, only with the vegetable oils EMPOL 1016, Dimer Acid Hydrogenated and Pripol 1009 it was possible to obtain stable latexes with adhesives properties. In Tables 9, 10 and 12 is shown a summary of the results obtained from the synthesis mentioned before. In the initial stage of the experiments synthesis was performed with an ionic surfactant (Dowfax 2A1) but it was observed that with this one in all reactions occurred some problems with coagulations, after changing the ionic surfactant to one nonionic (Disponil 1080) the problems with the coagulum formation was overcome. This fact can be explained as in this system exist so many charges and with an ionic surfactant it is so difficult to stabilize the emulsion during the polymerization. After this perception all reactions were performed with a nonionic surfactant (Disponil 1080).

**Table 9:** Summary of the experiments performed by emulsion polymerization with EMPOL 1016.

| Name of Polymer | Weight ratio = Empol:DMAEMA | %SC | % Emulsifier | Type of Emulsifier | % Coagulum |
|---|---|---|---|---|---|
| 1st Experiment | 1:1 | 25 | 3 | Dowfax 2A1 | 100 |
| PEDMAEMA 1 | 2:1 | 8 | 7 | Dowfax 2A1 | 6 |
| PEDMAEMA 2 | 2:1 | 16 | 4 | Dowfax 2A1 | 5 |
| PEDMAEMA 3 | 3:1 | 10 | 0 | Dowfax 2A1 | 100 |
| PEDMAEMA 4 | 3:1 | 13 | 2 | Dowfax 2A1 | 100 |
| PEDMAEMA 5 | 2:1 | 16 | 2 | Dowfax 2A1 | 100 |
| PEDMAEMA 6 | 2:1 | 9 | 4 | Disponil1080 | 0 |
| PEDMAEMA 7 | 2:1 | 15 | 4 | Disponil1080 | 0 |
| PEDMAEMA 8 | 2:1 | 17 | 4 | Disponil1080 | 0 |
| PEDMAEMA 9 | 1:1 | 11 | 4 | Disponil1080 | 0 |

**Table 10:** Summary of the experiments performed by emulsion polymerization with Dimer Acid hydrogenated.

| Polymer Name | Weight ratio = Dimer Acid:DMAEMA | % SC | % Emulsifier | Type of Emulsifier | % Coagulum |
|---|---|---|---|---|---|
| PDADMAEMA 1 | 1:1 | 5 | 4 | Disponil1080 | 100% Gel |
| PDADMAEMA 2 | 2:1 | 15 | 4 | Disponil1080 | 0 |
| PDADMAEMA 3 | 2:1 | 5 | 4 | Disponil1080 | 0 |
| PDADMAEMA 4 | 2:1 | 10 | 4 | Disponil1080 | 0 |
| PDADMAEMA 5 | 3:1 | 15 | 4 | Disponil1080 | 100% Coagulum |
| PDADMAEMA 6 | 4:1 | 15 | 4 | Disponil1080 | 100% Coagulum |
| PDADMAEMA 7 | 1.5:1 | 15 | 4 | Disponil1080 | 100% Gel |
| PDADMAEMA 8 | 2.5:1 | 15 | 4 | Disponil1080 | 100 |
| PDADMAEMA 9 | 1.75:1 | 10 | 4 | Disponil1080 | 0 |
| PDADMAEMA 10 | 2.25:1 | 10 | 4 | Disponil1080 | 0 |
| PDADMAEMA 11 | 1.75:1 | 15 | 4 | Disponil1080 | 0 |
| PDADMAEMA 12 | 2.25:1 | 15 | 4 | Disponil1080 | 0 |

**Table 11:** Summary of the experiments performed by emulsion polymerization with Pripol 1009.

| Polymer Name | Weight ratio = Pripol:DMAEMA | % SC | % Emulsifier | Type of Emulsifier | % Coagulum |
|---|---|---|---|---|---|
| PPDMAEMA 1 | 2:1 | 15 | 4 | Disponil1080 | 100 |
| PPDMAEMA 2 | 1.75:1 | 15 | 4 | Disponil1080 | 0 |

Analyzing the results obtained, it was possible to realize that only in an exactly relation, between the weight ratio relatively to the formulation of the monomer and the total solids contains, this system is reproducible. When, after the reaction, occurs less acid free (weight ratio of dimer acid: DMAEMA = 1:1) growth the formation of the gel, because the existence of more polymer inside the system. When the reverse case happens (more acid free after the polymerization and therefore less polymer inside the system) (weight ratio dimer acid: DMAEMA = 3:1) ensues coagulum formation. Relatively to the total solids contained in reaction it was difficult to carry out

polymerizations with this system through more than 20 percent. All dimer acids used in this study have high viscosity and high molecular weight, and when an increase of the percentage of the monomer occurs, in relation to the total weight, there was a similar growth in the viscosity of the system and it is impossible to stabilize the emulsions in these conditions. After this reflection it was possible to express that for obtaining stable latexes it is necessary to use a relation of the monomer between 1:1.75 to 1:2.25 with a ratio of solids contains concerning 10 to 20 percent. Figure 35 shows the final aspect of the latexes obtained with different relations amid the dimer acid and DMAEMA. Figure 36 illustrates a final film obtained with adhesive properties, using a monomer relation between EMPOL1016 to DMAEMA = 2:1.

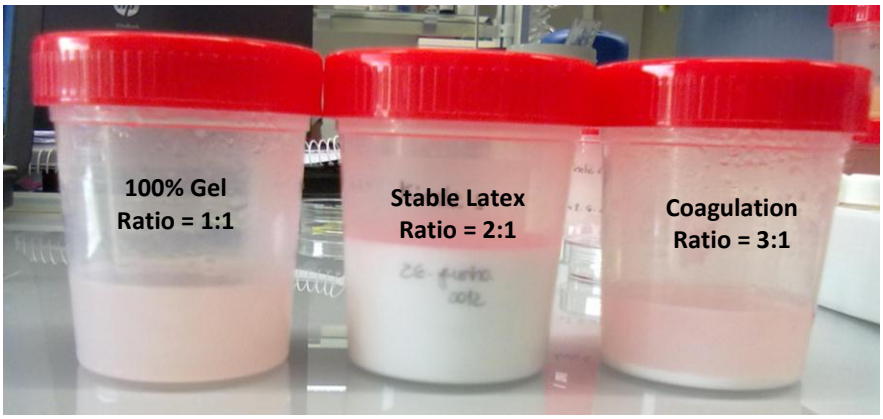



**Figure 35:** Final aspect of distinct latexes synthesized with dimer acid hydrogenated by different relations between the acid to DMAEMA.

**Figure 36:** Final film with adhesive properties, obtained using a monomer relation between EMPOL1016 to DMAEMA 2:1.

There were also performed some changes in the synthesis of the ionic monomer in order to study the influence of theses in the final adhesives properties. In all cases the final latexes obtained did not have notable adhesion ability. It will be necessary to carry out more investigations to understand more about this synthesis.

Table 12 presents a resume of the reactions performed in this experimental part of the work that do not work.

**Table 12:** Synthesis performed that doesn't work.

| **Monomer Synthesis** | | **Weight ratio Acid:IL** | **% SC** | **% Emulsifier** | **% Initiator** | **Type of emulsifier** | **Observations** |
|---|---|---|---|---|---|---|---|
| **Type of Acid** | **Type of IL** | | | | | | |
| Pripol 1040 (Trimer acid) | DMAEMA | 2:1 | 15 | 4 | 1 | Disponil 1080 | Some coagulum |
| Pripol 1040 (Trimer acid) | DMAEMA | 1:1.68 | 15 | 4 | 1 | Disponil 1080 | Some coagulum |
| Sun Flower Oil | DMAEMA | 1.75:1 | 15 | 4 | 1 | Disponil 1080 | Final latex with two phases |
| Pripol 2033 (diol) | DMAEMA | 2:1 | 15 | 4 | 1 | Disponil 1080 | Final latex with two phases |
| Dimer Acid | DMAEMA | 2:1 | 15 | 4 | 1 | Disponil 1080 | Final latex with two phases |
| Dimer Acid | DMAEMA | 0.6:1 (molar ratio) | 15 | 4 | 1 | Disponil 1080 | - |
| Dodecanodioic (Dimer Acid) | DMAEMA | 1:2 | 10 | 4 | 1 | Disponil 1080 | Water soluble polymer |

The adhesives properties of the stable latexes synthesized were investigated. The adhesive properties are characterized by an optimal balance of tack, peel resistance and shear strength properties. Table 13 presents the final results obtained for different dimer acids from distinct relations between dimer acid to DMAEMA. Analyzing the results obtained compared to others, achieved in the same conditions inside the POLYMAT group, it was possible to conclude that the relation 1:1.75 results in better adhesive properties comparatively to the other polymers synthesized with other weight ratios. In general all adhesives synthesized had good peel and this

translates notable adhesion in rigid surfaces at an angle of 180˚. It is necessary an average of 6 Newton to peel away a strip of tape. Relatively to the other values obtained in other measurements for the characterization of the adhesives properties were not so promising. The explanation stays in the chemical structure of the monomer, the ionic reticulation present in the structure of these doesn't produce strong mechanical properties and this fact elucidates the lower values of the probe tack measures. Relatively to the measures obtained for SAFT and Peel tests, it is possible to conclude that this type of adhesives does not resist so much time in high temperatures.

**Table 13:** Results of adhesives properties obtained from different dimer acids.

| **Polymer Name** | **$M_w$ (g/mol)** | **Weight ratio Acid:DMAEMA** | **Probe Tack (N/25 mm)** | **Loop Tack (N/25 mm)** | **Peel (N)** | **Shear Resistance (min) T=30˚C** | **SAFT (˚C)** |
|---|---|---|---|---|---|---|---|
| EMPOL 1016 | 590 | 25 | 0.078 | -0.23224 | 6.286 | 6 | <70 |
| EMPOL 1016 | | 8 | 0.055 | -0.01461 | 2.5411 | 25 | <70 |
| Dimer Acid | 570 | 16 | 0.24 | -0.26728 | 7.0767 | 66 | 65 |
| Dimer Acid | | 10 | 0.04652 | -0.2046 | 7.438 | 171 | 64 |
| Dimer acid | | 13 | 0.35 | -0.19 | 5.20 | 39 | 35 |
| Dimer acid | | 16 | 0.014 | -0.1331 | 4.574 | 122 | <70 |
| Pripol 1009 | 562 | 9 | 0.1878 | 0.0025 | 7,4244 | 115 | 67 |

For a better understanding of the kinetics of this type of system a study was carried out about the evolution of the conversion and the progress of the particle size during the reaction time.

Figure 37 represents the evolution of the conversion degree for PDADMAEMA4 during the polymerization, and Figure 38 presents the study about the evolution of the particle size for the same polymer.

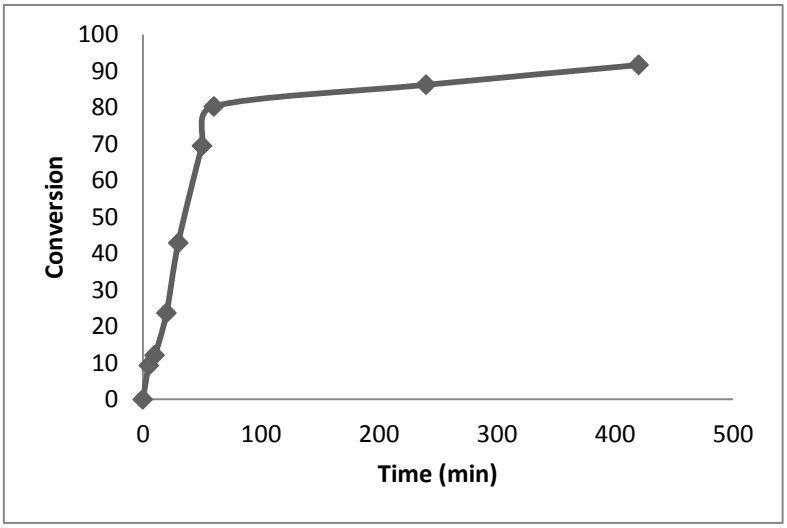



**Figure 37**: Evolution of the conversion degree for PDADMAEMA4 during the reaction time.

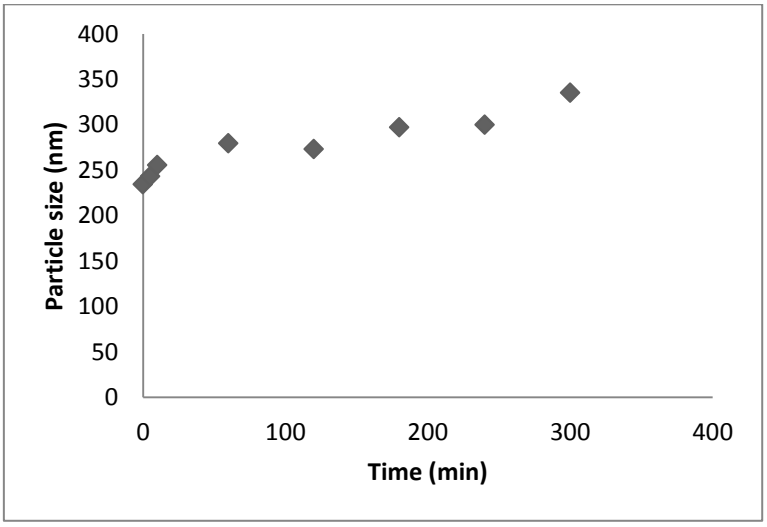



**Figure 38:** Evolution of the particle size for PDADMAEMA4 during the reaction time.

Analyzing the graph in Figure 36 it is possible to conclude that the efficiency of this reaction is very slow. In the first hours of the polymerization occurs a high increase of the conversion degree but after that, to obtain almost total conversion of the monomer (96%) it is necessary a prolongation of the polymerization for more than 8 hours.

For calculating the conversion degree during the polymerization was used the equation (5) and $^{1}$H NMR analysis. The partial depletion of the signals of the protons between 6.1 and 2.7 ppm (Figure 24) confirms the presence of free monomer in the final of the reaction and therefore was not obtained total conversion.

Investigating the evolution of the particle size during the polymerization time, it is possible to conclude that this increase during the first hours of the reaction, when the formation of the droplets occurs inside the system, after that constant diameter is generally maintained till the end of the polymerization, indicate good stability of the emulsion (Figure 38).

# Chapter 5

## 5.1 Conclusions:

Adhesives from renewable sources were successfully synthesized from ionic methacrylic-dicarboxylate monomers via emulsion polymerization by Free Radical Polymerization. When dicarboxylic acids were covalently attached, brittle films with low adhesive properties were obtained. After this initial study, we figure out that stable polymer latexes could be obtained by polymerization of methacrylic-carboxylate monomers at solids content less 20% and in a ratio of DMAEMA:Dicarboxylic acid between 1:1.75 and 1:2.25. The polymer films obtained by drying of the latexes showed relatively good adhesive properties. The adhesion for all adhesives synthetized, from different dimer acids and compositions were very similar without drawing any clear conclusions. The measurements of the peel resistance test demonstrate very promising adhesion values.

## 5.2 Future Work:

In a future investigation, the polymerization mechanism of the ionic monomers in water should be elucidated. It is also necessary to carry out a further investigation to characterize the final products obtained and try to improve the adhesive properties of them.

About the polymerization by covalent incorporation of carboxylic acids it is necessary to conduct a new study in order to eliminate the problems with the coagulum formation and also to improve the adhesive properties of the final films.

# Chapter 6

## 6.1 Bibliographic References:


**1** S. Ebnesajjad, "Handbook of Adhesives and Surface Preparation", Elsevier, **2011**, 8, 137-183.

**2** S. Ebnesajjad, "Handbook of Adhesives and Surface Preparation", Elsevier, **2011**, 8, 137-183.

**3** R. Vendamme, K. Olaerts, M. Gomes, M. Degens, T. Shigematsu, W. Eevers, "Interplay Between Viscoelastic and Chemical Tunings in Fatty-Acid- Based Polyesters Adhesives: Engineering Biomass toward Functionalized Step-Growth Polymers and Soft Networks", Biomacromolecules, **2012**.

**4** M. Moreno, M. A. Aboudzadeh, M. J. Barandiaran, D. Mecerreyes, "Facile Incorporation of Natural Carboxylic Acids into Polymers via Polymerization of Protic Ionic Liquids", Polymer Chemistry **2012**, 50, 1049-1053.

**5** L. M. Espinosa, M. A. R. Meier, "Plant oils: The perfect renewable resource for polymer science?!", European Polymer Journal, **2011**, 47, 837-852.

**6** D. Mecerreyes, "Polymeric ionic liquids: Broadening the properties and the applications of polyelectrolytes", Progress in Polymer Science, **2011**, 05, 007.

**7** P.M.Carrasco, A.R. Luzuriaga, M. Constantinou, P. Georgopanos, S. Rangou, A. Avegeropoulos, N. E. Zafeiropoulos, H. Grande, G. Cabañero, D. Mecerreyes, I. Garcia, "Influence of Anion Exchange in Self-Assembling of Polymeric Ionic Liquids Copolymers", Macromolecules, **2011**, 44, 4936-4941.

**8** A. Butté, G. Storti, M. Morbidelli, "Miniemulsion Living Free Radical Polymerization by RAFT", Macromolecules **2001**, 34, 5885-5896.

**9** G. Odian, "Principles of Polymerization, New York: Wiley-Interscience, 4$^{th}$ edition, **2004**.

**10** "Addition Polymerization", Material World Modules, **2009**.

**11** "Polymer Synthesis", Case Western Reverse University, **2009**.

**12** J. A. Pojman, J.Willis, D. Fortenberry, V. Ilyashenko, A. M. Khan, "Factors affecting propagation fronts of additions polymerization: Velocity, front curvature, temperature profile, conversion, and molecular weight distribution", Polymer Chemistry, **1995**, 33, 643-652.

**13** J. M. G. Cowie, V. Arrighi, "Polymers: Chemistry and Physics of Modern Materials", Scotland: CRC Press, 3rd edition, **2008**.

**14** J.M. Asua, "Emulsion polymerization: From Fundamental Mechanisms to Process Developments", Polymer Chemistry, **2004**, 42, 1025-1041.

**15** W. V. Smith, R. H. Ewart, "J. Chem. Phys.", **1948**, 16, 592.

**16** W. D. Harkins, "J. Am. Chem. Soc.", **1947**, 69, 1428.

**17** K. Landfester, "Polyreactions in Miniemulsions", Macromolecular Rapid Communications, **2001**, 22, 896-936.

**18** J. M. Asua, "Miniemulsion polymerization", Progress in Polymer Science, **2002**, 27, 1283-1346.

**19** Product Bulletin for Aerojet Accelerator, AMC-2. Rancho Cordova: Aerojet Chemicals **2000**.

**20** J. J. Scala, J. M. Sands, J. A. Orlicki, E. J. Robinette, G. R. Palmese, "Fatty acids-based monomers as styrene replacements for liquid molding resins, Polymer, **2004**, 45, 7729-7737.

**21** O. Mengal, G. Meunier, I. Cayré, K. Puech, P. Snabre, "TURBICAN MA 2000: multiple light scattering measurement for concentrated emulsion and suspension instability analysis", Talanta, **1999**, 50, 445.

**22** A. L. Elorza, "Design and Production of Waterborne Polyurethane/Acrylic Hybrid Pressure Sensitive Adhesives", University of Basque Country, **2010**, 293-305.

# APPENDICES

# Appendix I. Characterization Methods:

## I.1. Droplet and particle sizes:

The droplet and particle size and droplet and particle size distribution (PSD) were measured by dynamic light scattering (Nanosizer, Malvern). The equipment determines the particle size by measuring the rate of fluctuations in laser light intensity scattered by particles as they diffuse through a fluid.

Samples were prepared by diluting a fraction of the miniemulsion or latex in distilled water, saturated with monomers in the case of miniemulsion droplets in order to avoid droplet destabilization by thermodynamic reasons. The analysis was carried out at 25 ˚C and a run consisted in 1 minute of temperature equilibration followed by 2 size automatic measurements.

## I.2. Miniemulsion stability:

The miniemulsion stability was studied by analysing the evolution of the backscattered light using Turbiscan LAb$^{expert}$ device. The equipment reading head consists of a pulsed near infrared light source (880 nm) and two synchronous detectors. The transmission detector receives the light flux transmitted through the sample, while the backscattering detector measured the backscattered light. The detector head scans the entire length of the sample (55 mm) acquiring transmission and backscattered data every 40 µm. the curves obtained provide the transmitted and

backscattered light flux in percentage relative to standards (suspension of monodisperse spheres and silicon oil) as a function of sample height in mm.

This technique allows very easy visualization of creaming, sedimentation and coalescence/flocculation. Creaming occurs when the dispersed phase has a lower density than the continuous phase. It can be easily detected because the backscattering flux decreases at the bottom of the sample and increases at the top due to an increase in the disperse phase concentration. Sedimentation takes place when the density of the disperse phase is greater than the continuous one. In this case, the backscattering increases at the bottom of the sample due to an increase in the concentration. Coalescence/flocculation leads to the fusion of the interfaces increasing the droplet size. The particle size variation leads to a variation, usually a decrease of the backscattering over the whole height of the sample.

## I.3. Conversion:

Monomer conversion could not be measured gravimetrically due to the high boiling point of the monomer and therefore $^{1}$H-NMR spectroscopy was employed. Samples were recorded using a 500 MHz 1H-NMR BrukerDRX-500 spectrometer.

The addition to the sample of 1,3,5-bencenetricarboxylic acid (BTC) as internal standard allows the determination of the absolute concentration of residual monomer by means of a calibrate. To prepare the $D_2O$-BTC solution, BTC was dissolved in NaOH 1M and then neutralized with HCl and diluted with water.

# Appendix II. Fatty Acids Properties:

## II.1 EMPOL 1016

| | | |
|---|---|---|
| **Composition HPLC** | % Monobasic Acid | 4 |
| | % Dibasic Acid | 80 |
| | % Polybasic Acid | 16 |
| **Specifications** | $M_w$ (g/mol) | ≅589.67 |
| | Acid Value (mg KOH/g) | 190-198 |
| | Appearance Visual | Clear liquid |
| | Viscosity (140 ˚F, cSt) | 450-510 |

## II.2 Dimer Acid Hydrogenated:

| | | |
|---|---|---|
| **Specifications** | $M_w$ (g/mol) | ≅570 |
| | Acid Value (mg KOH/g) | 194-198 |
| | Density (g/mL at 25˚C (lit.)) | 0.95 |
| | Viscosity (mPa.s at 25˚C (lit.)) | 8000 (typ) |

## II.3 Pripol 1009:

| | | |
|---|---|---|
| **Specifications** | $M_w$ (g/mol) | ≅562.92 |
| | Acid Value (mg KOH/g) | 194-198 |
| | Viscosity (mPa.s at 25˚C (lit.)) | 7500 (typ) |

## II.4 Pripol 1040

| | | |
|---|---|---|
| **Specifications** | $M_w$ (g/mol) | ≅843.36 |
| | Acid Value (mg KOH/g) | 184-194 |
| | Viscosity (mPa.s at 25˚C (lit.)) | 45000 (typ) |

## II.5 Pripol 2033

| | | |
|---|---|---|
| **Specifications** | $M_w$ (g/mol) | ≅534.95 |
| | Hydroxyl Value (mg KOH/g) | 202-212 |

## II.6 Sunflower Oil

| | | |
|---|---|---|
| **Composition** | Palmitic Acid | 4-9% |
| | Stearic Acid | 1-7% |
| | Oleic Acid | 14-40% |
| | Linoleic Acid | 48-74% |
| **Specifications** | Density (25˚C) (kg/$m^3$) | 918.8 |
| | Flash Point (˚C) | >110 |
| | Free Fatty Acid | ≤ 0.13% |

## II.7 Dodecanedioic acid

| | | |
|---|---|---|
| **Specifications** | $M_w$ (g/mol) | 230.30 |
| | Flash Point (˚C) | 220 |

# Appendix III. Ionic Liquids Properties:

## III.1 2-(Dimethylamino) Ethyl Methacrylate (DMAEMA):

| | | |
|---|---|---|
| **Specifications** | $M_w$ (g/mol) | 157.21 |
| | Toxity (acute oral LD50,rats, mg/kg) | 1500 |
| | Viscosity (CPS at 20 ˚C) | 1.34 |
| | Freezing Point (˚C) | Below -60 |
| | Flash Point (˚C) | 65 |

## III.2 2-(Dimethylamino) Ethyl Acrylate (DMAEA):

| | | |
|---|---|---|
| **Specifications** | $M_w$ (g/mol) | 143.18 |
| | Toxity (acute oral LD50,rats, mg/kg) | 455 |
| | Relative Density ($g/cm^3$ at 25 ˚C ) | 0.94 |
| | Melting Point (˚C) | -80 |
| | Boiling Point (˚C) | 172.5 |